ELECTRON TRANSFER REACTIONS BETWEEN 1,10-PHENANTHROLINE COMPLEXES OF CHROMIUM(II) AND CHROMIUM(III)

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SUMMARY

The reaction between $Cr(L)_3^{3+}$* and $Cr(L)_3^{2+}$ has been studied. The initial rate obeys a one term rate law $-d(Cr(L)_3^{3+})/dt=k_1(Cr(L)_3^{2+})$. The rate constant, k_1, is related to a first order dissociative process of $Cr(L)_3^{2+}$ leading to the formation of $Cr(L)_2(S)_2^{2+}$.** The mechanism of the reaction is best described as

$$CrL_3^{2+} + 2S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CrL_2S_2^{2+} + L$$

$$CrL_3^{3+} + CRL_2S_2^{2+} \xrightarrow{k_3} CrL_3^{2+} + CrL_2(S)_2^{3+}$$

When the solvent is water, the rate of formation of the diaquobis (1,10-phenanthroline)chromium(III) is measured by following the increase in the absorbance at 525 nm. Assuming that there is a steady state concentration of $CrL_2(aq)_2^{2+}$ and that $k_3(CrL_3^{3+})$ is much greater than $k_2(L)$, the rate is then equal to $k_1(CrL_3^{2+})$. The value of k_1 was determined to be 0.0803 $sec.^{-1}$ at 26.5°C. The activation energy was found to be 22.5 Kcal./mole.

The proposed mechanism may be tested by measuring the rate constant for the dissociation of CrL_3^{2+} in high acid concentration, which

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*Where L = 1,10-phenanthroline

**Where S = solvent

should be the same as the rate found above. The rate constant for acid dissociation of CrL_3^{2+} in 0.1 N HCl was found to be 0.081 sec.$^{-1}$, in excellent agreement with the proposed mechanism.

Optical isomers of CrL_3^{3+} were resolved by a known method. The initial rate of loss of optical activity of CrL_3^{3+} when reacted with CrL_3^{2+} was found to be first order in CrL_3^{2+} and zero order in CrL_3^{3+}. The calculated initial rate constant, evaluated from a linear plot of rotation versus time was approximately two and a half times larger than the initial rate constant for the hydrolysis reaction. The rotation at any time is directly proportional to the concentration of d-CrL_3^{3+}. The initial rate for the loss of optical activity was best described by the plot of the log of the rotation versus time; while the initial rate of hydrolysis was described by the linear plot of concentration of CrL_3^{3+} versus time.

Besides the hydrolysis reaction, a parallel reaction between $CrL_3^{2+}$and CrL_3^{3+} is taking place; this reaction is the exchange reaction. The exchange reaction was found to be first order in CrL_3^{2+} and zero order in CrL_3^{3+}. Before $CrL_3^{2+}$and CrL_3^{3+} can exchange an electron, the CrL_3^{2+} must be activated in the rate determining step. The literature contains evidence that water molecules are bound between the 1,10-phenanthroline rings in the CrL_3^{2+} complex. The best model for the activated complex involves removal or rearrangement of these water molecules prior to electron transfer with CrL_3^{3+}. The initial first order rate constant for the activation of CrL_3^{2+} was found to be 0.134 sec.$^{-1}$ at 25.8°C, with an activation energy of 27.2 Kcal./mole and an entropy of activation of 28 cal./mole deg.

CHAPTER I

INTRODUCTION

The topic of this study is redox reactions between metal complexes. For redox reactions of metal complexes in aqueous solution, two mechanisms have been postulated, the inner sphere and the outer sphere.[1] The inner sphere of a complex refers to the set of ligands directly bonded to the metal ion. In the inner sphere mechanism at least one of the ligands is bonded to both of the reactants in the activated complex. In the outer sphere mechanism there is no commonly bonded ligand in the activated complex. The reader is referred to the literature for a discussion of the innter sphere reaction mechanism.[2,3,4,5]

When the oxidant and reductant differ only in the oxidation state of the central metal ion, the exchange of an electron or electrons produces products that are identical to the initial reactants. Such a reaction is called an exchange reaction. For a one electron transfer, the exchange reaction may be written generally as

$$ML_n^{+m} + ML_n^{+(m+1)} \longrightarrow ML_n^{+(m+1)} + ML_n^{+m} \qquad (1)$$

where M is the central metal atom and L is the attached ligand.

It is the purpose of this investigation to elucidate some of nature's secrets about the factors that influence the rate of the exchange reaction that proceeds by the outer sphere mechanism.

The outer sphere mechanism has been the subject of several theoretical treatments.[6,7,8,9,10] The one proposed by Marcus has been the

one most widely accepted.[6] Marcus's treatment has as one of its essential features the Franck-Condon Principles. This principle states that internuclear distances do not change during an electron transition. The reorganization of solvent and the reorganization of internuclear distances of the reacting molecules in the process of forming the activated complex is needed immediately before the transfer of an electron. Marcus's theory involves the a priori calculation of this reorganization energy. The theory assumes that changes in the bond distances occur by vibrational transitions. This requires experimental knowledge of the force constants involved. Though approximations can be made, the general lack of knowledge of the required force constants hinders significantly the a priori calculations.[6] Generally it can be said that the greater the difference in the metal-ligand bond distances for the reactants in an exchange reaction, the greater will be the energy requirement to compress and stretch these bonds, and the slower the rate is expected to be. The theory is used to estimate the rate constant for a redox reaction using rate constants of related exchange reactions.[7] The redox reaction

$$Ox_1 + Red_2 \xrightarrow{k_{12}} Ox_2 + Red_1 \qquad (2)$$

is related to the two exchange reactions

$$Ox_1 + Red_1 \xrightarrow{k_{11}} Ox_1 + Red_1$$

$$Ox_2 + Red_2 \xrightarrow{k_{22}} Ox_2 + Red_2$$

The rate constant k_{12} for Eq. 2 may be estimated if we know (1) the rate constants, k_{11} and k_{22}, for the exchange reactions, and (2) the

equilibrium constant K_{12} for Eq. 2. If the coulombic work terms cancel, then $k_{12} = (k_{11}k_{22}k_{12}f)^{\frac{1}{2}}$; where $f=(\ln K_{12})^2/4\ln(k_{11}k_{22}/Z^2))$ and Z is the collision frequency. The "f" term is often within an order of magnitude of unity. Table 1[2,11] lists the various experimental and predicted k_{12}. The fit has been recognized as good, except for the reactions involving cobalt.

Another quantitative use of Marcus's theory has been to calculate the entropy and enthalpy of activation of the exchange reaction.[9] The exchange reaction allows one to simplify the mathematical expressions and there is greater likelihood of cancellation of the work terms than in reactions involving different complexes. The calculated values of the enthalpy and entropy of activation show deviations from the expected value of the divalent and trivalent ions of the first transition series.[9] The deviations were speculated to be caused by Crystal Field effects.[9] Crystal Field Stabilization Energy has been included in Marcus's treatment by Hush; however, as with the force constants, the CFSE terms are difficult to calculate a priori.[6]

From the study of many redox reactions one general rule has been found. For a one equivalent change in which a t_{2g} electron in the reductant is transferred to a t_{2g} orbital of the reduced product, the reaction is always fast.[13] See Table 2.[12] Adding an electron to or removing an electron from the t_{2g} non-binding orbital is energetically easy compared to the same operation for an e_g orbital because the change in the ligand - metal bond distance is expected to be small for adding or removing a t_{2g} electron. Since an e_g electron is in an antibonding orbital, it has a greater effect on the ligand - metal bond distance.

Table 1. Calculated and Observed Values for some Redox Reactions

Reductant	Oxidant	k_{12} observed	k_{12} calculated
Fe(II)	Ce(IV)	1.3×10^{6}	6×10^{5}
Cr(II)	Fe(III)	$\approx 8 \times 10^{3}$	$\leq 6 \times 10^{5}$
V(II)	Fe(III)	$> 10^{5}$	9×10^{5}
Eu(II)	Fe(III)	$> 10^{5}$	$\leq 2 \times 10^{6}$
$Fe(CN)_6^{4-}$	Ce(IV)	1.9×10^{6}	6×10^{6}
$Mo(CN)_8^{4-}$	Ce(IV)	1.4×10^{7}	1.3×10^{7}
$W(CN)_8^{4-}$	$IrCl_6^{2-}$	6.1×10^{7}	8.1×10^{7}
$Fe(CN)_6^{4-}$	$IrCl_6^{2-}$	3.8×10^{5}	5.7×10^{5}
Fe(II)	Mn(III)	1.5×10^{4}	3×10^{4}
Cr(II)	Co(III)	$> 3 \times 10^{2}$	$\leq 10^{10}$
V(II)	Co(III)	$> 3 \times 10^{2}$	$\approx 2 \times 10^{10}$
Fe(II)	Co(III)	42	6×10^{6}
$Ru(NH_3)_6^{2+}$	Fe(III)	3.4×10^{5}	7.5×10^{6}
V(II)	$Ru(NH_3)_6^{3+}$	82	4.2×10^{3}
V(II)	$Co(NH_3)_6^{3+}$	3.3×10^{-3}	$< 1.5 \times 10^{-4}$
$Ru(NH_3)_6^{2+}$	$Co(NH_3)_6^{3+}$	1.2×10^{-2}	$< 3 \times 10^{-7}$

Table 2. Some Second Order Rate Constants for a Transfer of a t_{2g} Electron by an Outer Sphere Mechanism*

Reductant	Oxidant	Rate Constant 1./mole sec.
$Fe(CN)_6^{4-}$	$Fe(CN)_6^{3-}$	7.4×10^2
$Fe(CN)_6^{4-}$	$Fe(phen)_3^{3+}$	10^8
$Fe(phen)_3^{2+}$	$Fe(phen)_3^{3+}$	10^5
$IrCl_6^{3-}$	$IrCl_6^{2-}$	10^3
$Os(bipy)_3^{2+}$	$Os(bipy)_3^{3+}$	5×10^4
$Ru(phen)_3^{2+}$	$RhCl_6^{2-}$	2.5×10^9
$Fe(phen)_3^{2+}$	$Co(H_2O)_6^{3+}$	1.4×10^4
$Fe(CN)_6^{4-}$	$IrCl_6^{2-}$	3.8×10^5
$Cr(bipy)_3^{2+}$	$Co(NH_3)_6^{3+}$	6.9×10^2
$Cr(bipy)_3^{2+}$	$(Co(NH_3)_5H_2O)^{3+}$	5×10^4
$Cr(bipy)_3^{2+}$	$(Co(NH_3)_5F)^{2+}$	1.8×10^3
$Cr(bipy)_3^{2+}$	$(Co(NH_3)_5Cl)^{2+}$	8×10^5
$Cr(bipy)_3^{2+}$	$(Co(NH_3)_5Br)^{2+}$	5×10^6
$Ru(NH_3)_6^{2+}$	$(Co(NH_3)_5Br)^{2+}$	1.6×10^3
$Fe(H_2O)_6^{2+}$	$Fe(dipy)_3^{3+}$	2.7×10^4
$Fe(H_2O)_6^{2+}$	$Fe(phen)_3^3$	3.7×10^4

*Data taken from Reference 12.

The ligand - metal bond distances in the reduced and the oxidized states will be different when the two states differ by an e_g electron. As mentioned earlier, the greater the difference in bond lengths between the reactants in the exchange reaction, the larger the reorganization energy and the slower the rate will be.

Another factor is the distance between the reacting metal complexes at the time of electron transfer is also significant.[6,7] It has been possible to surround the metal center such that it is very difficult for the electron to penetrate the ligand. The exchange reaction between heteropoly tungstate complexes of Co(II) and Co(III) is such an example. The cobalt ions are both high spin, tetrahedrally coordinated in $CoO_4W_{12}O_{36}^{6-}$ and $CoO_4W_{12}O_{36}^{5-}$ and the second order rate constant observed is 10^{-3}, while 10^3 was predicted by Marcus's theory.[14]

The effect of changing the ligand on the metal ion can cause significant changes in the rate constant for the exchange reaction. For the iron(II)/iron(III) exchange[15] we have:

$Fe(H_2O)_6^{2+}/Fe(H_2O)_6^{3+}$	4.0	1/mole sec.
$Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$	> 40	1/mole sec.
$Fe(phen)_3^{2+}/Fe(phen)_3^{3+}$*	> 10^5	1/mole sec.

In each of the cases a t_{2g} electron is tranferred. Cyanide and 1,10-phenanthroline are both known to π back bond. The electrons are in effect delocalized to a greater extent than for water. For the 1,10-

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*(where phen = 1,10-phenanthroline)

phenanthroline case, the delocalization mechanism can be pictured as a means for the exchanging electron to migrate to the perimeter of the molecule and thus facilitate the transfer of the electron.

It was cited previously that redox reactions involving cobalt did not conform to the prediction of the Marcus theory. It has been claimed[16] that the discrepancy is due to abnormal values for the related cobalt exchange reaction. Listed below are the second order rate constants for four Co(II)/Co(III) exchange reactions at 25°C.[15]

$Co(H_2O)_6^{2+}/Co(H_2O)_6^{3+}$	3	1/mole sec.
$Co(NH_3)_6^{2+}/Co(NH_3)_6^{3+}$	10^{-9}	1/mole sec.
$Co(en)_3^{2+}/Co(en)_3^{3+}$*	10^{-5}	1/mole sec.
$Co(phen)_3^{2+}/Co(phen)_3^{3+}$	15	1/mole sec.

In all cases the Co(II) is high spin, with configuration $(t_{2g})^5(e_g)^2$, and the Co(III) is low spin, with configuration $(t_{2g})^6$.

For some time it was thought that the slow case could be explained by large differences in the bond distances between $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$. However, Ibers et al.[17] determined the Co-N bond distances for the complexes and found the difference to be only 0.178Å. He later[18] presented a calculation of the activation energy of the exchange reaction assuming that the cobalt(II) complex is electronically excited from the high spin state to the low spin state. Basolo and Pearson[19] argue that the reason why the aquo and 1,10-phenanthroline cases are relatively fast compared to the ammonia and ethylenediamine cases is that at extreme low and high ligand field strengths, the energy

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*(where en = ethylenediamine)

for electronic excitation is lower. Beattie et al.[20,21] have recently indicated the relaxation of the excited states of transition metal complexes are probably too fast for the excited state to be involved in the rate determining step in most electron exchange reactions.

Endicott et al.[22] argue that for the ammonia case there is a reorganizational energy barrier that results from the Jahn-Teller distortion accompanying the localization of electron density in a d_{z2} orbital in the low-spin cobalt(II) intermediate. In a different paper Endicott et al.[15] concluded that for cobalt(II)/cobalt(III) exchange reactions there is a breakdown in the assumptions used to derive Marcus's relationships that were cited earlier. Further research seems necessary before any general conclusion can be stated for the irregular behavior of the cobalt case.

The complications that arise in the cobalt case are not expected to arise in the study of chromium complexes.* There are numerous studies in which Cr^{2+} has been used as a reductant, and several using low spin $Cr(bipy)_3^{2+}$.** Taube et al.[24] and Halpern et al.[25] have studied the reduction of cobalt ammines by $Cr(bipy)_3^{2+}$; Beattie and Basolo[26] studied the reduction of Platinum(IV) ammines with $Cr(bipy)_3^{2+}$; Farina and Wilkins[27] report a rate constant of greater than 3×10^6 1./mole sec. (reaction completed in time of mixing) for the reaction of $Cr(bipy)_3^{2+}$ with bis(2,2',6',2''-terpyridine)Chromium(III). Sutter and

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* Chromium(III) has only one spin arrangement possible in an octahedral ligand field.

** (where bipy = 2,2-bipyridine)

Hunt[28] report that $Cr(phen)_3^{2+}$ reacts with optically active $Co(phen)_3^{3+}$ to give optically active $Cr(phen)_3^{3+}$.

However there are only two reported rates for the exchange reaction involving the oxidation of Cr(II) by Cr(III). Anderson and Bonner[29] report for the hexaaquochromium(II)/(III) exchange, a rate of less than or equal to 2×10^{-5} 1./mole sec.; Stranks[30] reports the enthalpy and entropy of activation for the $Cr(urea)_6^{2+}/Cr(urea)_6^{3+}$ exchange. From these data a rate of 10^{-7} 1./mole sec. is calculated for 25°C. $Cr(H_2O)_6^{2+}$ and $Cr(urea)_6^{2+}$ are high spin, $(t_{2g})^3(e_g)$, therefore an e_g electron is being transferred.

The nature of the hexaaquo system studied by Anderon and Bonner[29] permitted only a limit to the exchange to be set. Stranks[30] has not reported in detail his study of the urea system. In effect there has been no reported detailed study of a chromium(II)/chromium(III) exchange reaction.

It is the purpose of this work to attempt to measure the exchange reaction between the tris 1,10-phenanthroline complexes of chromium(II) and chromium(III) ions. Since it is known that the $Cr(phen)_3^{2+}$ is low spin[31], the electron is transferred from a t_{2g} orbital into another t_{2g} orbital; because of this the rate is expected to be faster than for the aquo or urea cases. Also pi back bonding of the phenanthroline ligand should assist in "conducting" the electron and thereby increase the rate as compared to the hexaaquo or hexaurea cases. The fast rate reported by Farina and Wilkins[27] for the transfer of a t_{2g} electron between $Cr(bipy)_3^{2+}$ and $Cr(terpy)_3^{3+}$* would justify the prediction.

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*(where terpy = 2,2',6',2''-terpyridine)

It is known that optically active $Co(phen)_3^{3+}$ reacts with $Cr(phen)_3^{2+}$ to yield optically active $Cr(phen)_3^{3+}$.[28] La Mar and Van Hecke[40] have argued that this stereospecific reaction is due to the manner in which water is bound in the secondary coordination sphere of $Cr(phen)_3^{2+}$. If such is the case then the water in the secondary coordination sphere of $Cr(phen)_3^{2+}$ could play a significant role in the electron transfer rate with $Cr(phen)_3^{3+}$.

Methods of Studying the Exchange Reaction

In order to measure the rate for an exchange reaction, one must use some form of labelling since the products are the same as the reactants. Traditionally labelling has been done with radioactive isotopes.[6] The technique requires chemical or physical separation of the reactants in which care must be taken to avoid separation induced exchange. Because of the time needed for separations the technique is limited to relatively slow reaction. Methods of measuring the exchange reaction not requiring separation are (1) nmr spectroscopy, (2) epr line broading, and (3) labelling with an optically active reactant.[15]

The following systems have been studied by both the radiochemical and the optical activity methods:

(1) $Co(en)_3^{2+}/Co(en)_3^{3+}$. The radiochemical study of Lewis et. al.[32] was verified by Dwyer and Sargeson[33] using the optical activity method.

(2) $Co(EDTA)_3^{2-}/Co(EDTA)_3^{1-}$. The Adamson and Vorres[34] radiochemical study was verified by the optical activity study of Im and Busch.[35]

(3) $Fe(phen)_3^{2+}/Fe(phen)_3^{3+}$ studies by radiochemical[36], nmr[37], and optical activity[36] techniques have given similar results in that the reaction is too fast to measure (rate constant $> 10^5$).

(4) $Os(bipy)_3^{2+}/Os(bipy)_3^{3+}$ has been studied by the radiochemical, optical activity, and nmr techniques and all gave similar results, that the reaction is fast.[36]

(5) $Co(phen)_3^{2+}/Co(phen)_3^{3+}$ has been studied by both the radiochemical and optical activity methods by Gorton.[38] The radiochemical technique gave a complex rate expression. The rate measured by the optical activity method gave a simple first order dependence in both of the reactants. The second order rate constant for the electron exchange reaction was determined to be 6.35 l./mole sec. by the optical activity technique and 1.13 l./mole sec. by the radiochemical technique.*

The overall conclusion can be made that the optical activity method can be successfully used to determine the rate of favorable electron exchange reaction.

Hunt et al.[39] have reported the resolution of $Cr(phen)_3^{3+}$. Langford et al.[41] report a partial photoresolution of $Cr(phen)_3^{3+}$, using an analog of the Pfeiffer Effect. They also report a half life of 17 days at 25°C for thermal racemization. The $Cr(phen)_3^{2+}$ ion is configurationally labile. Im and Busch[35] have demonstrated that for such a system the use of optical activity as a label is feasible for the study of electron exchange reactions. It is proposed that the optical

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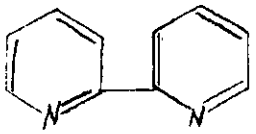
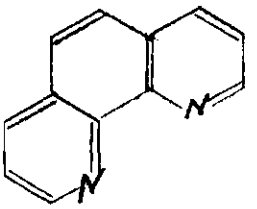
*The value determined by the optical activity method is considered to be more reliable.[71]

activity method be used for the study of the exchange reaction between $Cr(phen)_3^{2+}/Cr(phen)_3^{3+}$.

The remainder of this introduction will be concerned with a review of the known studies of $Cr(phen)_3^{2+}$ and $Cr(phen)_3^{3+}$. Studies of the $Cr(bipy)_3^{2+}$ and $Cr(bipy)_3^{3+}$ will be referred to also because of the structural similarity between 2,2'-bipyridine (I) and 1,10-phenanthroline (II).



(I)



(II)

A review of 2,2'-bipyridyl and 1,10-phenanthroline complexes by McWhinnie and Miller[42] appeared in 1969. Garner and House[43] have published a review of the ammine complexes of chromium(III).

Spectral Studies

Besides reporting the resolution of $Cr(phen)_3^{3+}$, Hunt et al.[39] also report the ORD spectrum of the compound. Kane-Maguire et al.[44] and Mason et al.[45] discuss the circular dichroism spectrum and the uv-visible spectra of d-$Cr(phen)_3^{3+}$.

I. Fujita et al.[46] have measured the CrL_3^{2+} (where L = bipy or phen) spectrum from 200 nm to 1200 nm. For $Cr(phen)_3^{2+}$ the visible and near infrared peaks at 1100, 810, and 480 nm are assigned to metal to ligand charge transfer transitions. Konig and Herzog[47] reached a similar conclusion in 1969 for the spectra peaks of $Cr(bipy)_3^{2+}$ in the visible.

Magnetic Studies

Magnetic studies of salts containing CrL_3^{2+} have caused a controversy as to the cause of the magnetic moment being close to the spin only value of 2.83 B.M. The Cr(II) ion in these complexes has a low spin configuration and values higher than spin only are expected due to incomplete quenching of the orbital contribution.

A. Earnshaw et al.[31] argued that the values observed in a temperature dependent study, (80° to 300°K), of the magnetic moment can probably be explained by both (a) delocalization of the metal t_{2g} electron onto the ligand, and (b) the presence of low symmetry components in the ligand field, caused by either the Jahn-Teller Effect or by atoms outside the immediate coordinated sphere. Terezakis and Carlin[48] in examining the $Cr(bipy)_3^{2+}$ ion concluded that the magnetic moment could be accounted for by the delocalization of the metal t_{2g} electron onto the ligand. The assumption of octahedral symmetry was used in these studies. Udachin and Dyatkina[49] on the basis of MO calculations concluded that the data could be better explained by trigonal distortion. Lutz et al.[50] extended the studies of the magnetic moment to 20°K and concluded that there is significant deviation from cubic symmetry.

NMR Studies

In their initial report, La Mar and Van Hecke[51] argued, on the basis of nmr measurements of $Cr(phen)_3^{2+}$ and $Cr(bipy)_3^{2+}$, that there is trigonal distortion of the geometry of the complex and that the delocalization of the electrons does not take place. However, in two more recent papers, La Mar and Van Hecke[40,52], on the basis of further nmr

measurement and molecular orbital calculations, reversed themselves on whether the unpaired electrons are delocalized. La Mar[53] concludes that (1) extensive π bonding is present; (2) both metal to ligand and ligand to metal charge transfer delocalization mechanisms are operative, though the net spin transfer is small; (3) the spin only magnetic moment of these chelates probably arises from the trigonal distortion.

Solution Study

Hunt has estimated the various equilibrium constants between chromium(II) and 1,10-phenanthroline in aqueous solution.[54] When chromium(II) and 1,10-phenanthroline are mixed, the following complexes are formed: CrL^{2+}, CrL_2^{2+}, and CrL_3^{2+}. The following equilibrium constants were calculated using potentiometric titration data:

$$K_1 = CrL^{2+}/(Cr^{2+})(L) = 1.29 \times 10^9 \quad (3)$$

$$K_2 = CrL_2^{2+}/(CrL^{2+})(L) = 5.00 \times 10^6 \quad (4)$$

$$K_3 = CrL_3^{2+}/(CrL_2^{2+})(L) = 1.59 \times 10^5 \quad (5)$$

From these values, it can be seen that in a tenfold excess of 1,10-phenanthroline, the tris complex will be the dominant species. Similar values are found for the Cu(II) and Zn(II) complexes.[55]

Electrochemistry

The electrochemistry of the $Cr(bipy)_3^{3+}$ ion has been the subject of several reports. Vlcek's[56] initial report on the polarography of $Cr(bipy)_3^{3+}$ has been found in error by Baker and Mehta[57] and Tucker

et al.[58] Baker and Mehta concluded that the polarograms could be interpretated by the following mechanism. The CrL_3^{3+} is reduced to CrL_3^{2+} at $E_{1/2}$ = -0.49 V (versus SCE). In order to explain the reduction wave at $E_{1/2}$ = -0.72 V. the following mechanism was proposed:

$$CrL_3^{2+} + 2H_2O \underset{k-1}{\overset{k1}{\rightleftharpoons}} CrL_2(H_2O)_2^{2+} + L \qquad (6)$$

$$CrL_2(H_2O)_2^{2+} + CrL_3^{3+} \xrightarrow{k2} CrL_2(H_2O)_2^{3+} + CrL_3^{2+} \qquad (7)$$

$$CrL_2(H_2O)_2^{3+} + e^- \longrightarrow CrL_2(H_2O)_2^{3+} \quad E_{1/2} = -0.72 \text{ V.} \qquad (8)$$

They identified the product $Cr(bipy)_2(H_2O)_2^{3+}$ from the reported spectrum. They report a rate constant for k_1 as 0.38 $sec.^{-1}$ at 25°C, and an activation energy of 22.6Kcal./mole. The rate constant is identical to that determined by acid dissociation as reported by Halpern et al.[59] Soignet and Hargis[60] verified the polarographic study of Baker and Mehta and extended the study to include controlled-potential electrolysis and cyclic voltammetric techniques. The mechanism proposed is the same as that of Baker and Mehta; however Soignet and Hargis report a rate constant for the dissociation of $Cr(bipy)_3^{2+}$ of 0.107 $sec.^{-1}$ at 23°. The rate constant is derived from the cyclic voltammetry data.

Soignet and Hargis[61] report the only electrochemistry study of $Cr(phen)_3^{3+}$. The proposed mechanism is identical to that for the bipyridine complex. They report a rate constant for the dissociation of

$Cr(phen)_3^{2+}$ of 0.015 sec.$^{-1}$ at 25°. McCray and Sturrock[62] found that 1,10-phenanthroline is heavily adsorbed on the electrode surface. This observation questions the quantitative results of Soignet and Hargis.

Additional Proposal

Since the electrochemistry studies of Soignet and Hargis indicate that $Cr(phen)_2(H_2O)_2^{3+}$ is formed in solutions containing $Cr(phen)_3^{2+}$ and $Cr(phen)_3^{3+}$, the exchange reaction will most certainly be accompanied by the Cr(II) catalyzed hydrolysis of the Cr(III) reactant. It will therefore be necessary to study this reaction also for a complete understanding of the system. The rate of formation of $Cr(phen)_2(H_2O)_2^{3+}$ will be determined spectrophotometrically when $Cr(phen)_3^{2+}$ and $Cr(phen)_3^{3+}$ are mixed.

There are definite reasons to question the work of Soignet and Hargis on the rate constant reported for the dissociation of $Cr(phen)_3^{2+}$, as discussed previously. In order to test their report, it is proposed that the rate of dissociation of $Cr(phen)_3^{2+}$ be measured in high acid concentrations by spectrophotometric technique.

CHAPTER II

EXPERIMENTAL

Chemicals

1,10-phenanthroline monohydrate was obtained from several suppliers and was used as received.

The following chemicals were purchased as reagent grade and were utilized without further purification:

acetone

ammonium hydroxide

ammonium persulfate

bromine

calcium chloride

chloroform

chromium(III) nitrate "n" hydrate

chromium(III) sulfate "n" hydrate

hydrogen peroxide

iodine

iron(II) chloride hexahydrate

mercuric chloride

potassium chloride

potassium dichromate

potassium hydroxide

potassium nitrate

silver nitrate

sodium hydroxide

vanadium pentoxide

hydrochloric acid

nitric acid

sulfuric acid

Sodium perchlorate was obtained from Fischer Chemical Company and was used without further purification.

Ethanol was either 95 percent or absolute and was utilized without treatment.

Chlorine was acquired from Tesco Chemical Company and used without further purification.

Zinc metal was treated with 1 M hydrochloric acid and rinsed throughly prior to use.

Dowex 50W-4X cation exchange resin was washed with 3 M HCl and rinsed with water until no precipitate was observed with the addition of silver nitrate.

Dowex2-X8 anion exchange resin (same as for 50W-4X).

Potassium antimonyl tartrate was purchased from Fischer Chemical Company and used as received.

Water was distilled from basic permanganate prior to use.

Description of the Oxygen Purging Systems

Chromium(II) compounds are air sensitive. There are reports that solid chromium(II) compounds are stable for days in dry air. It was throught best to avoid the possibility of contamination by performing

our operations involving chromium(II) compounds in an inert atmosphere. General anaerobic techniques are described elsewhere. Described below are the glove box used and the oxygen scrubbing line used for bench top operations.

The Manostat Glove Box was equipped with a Welch Model 1400B Duo-Seal Pump and a UGA, U.S. pressure gauge on the portal. A Dyna-Vac circulating pump outside the box circulated the atmosphere through oxygen scrubbing towers that used MnO as an oxygen scavenger. The prepurified nitrogen gas was also passed through an oxygen scrubbing tower prior to entering the glove box. The glove box was continually swept with purified nitrogen and a positive pressure of approximately 2 cm. of glycerol was maintained at all times. Prior to use, the atmosphere was circulated for two hours through the oxygen scrubbing towers.

For operations on the bench top, a nitrogen gas stream was provided by passing prepurified nitrogen gas through a desiccant, an oxygen scrubbing tower (same as above), a vanadium(II) trap, and a concentrated sulfuric acid trap. The desiccant was indicating Drierite. The vanadium(II) trap was made by mixing amalgamated zinc metal (0.25% Hg) with sulfuric acid and vanadium pentoxide. After several hours of nitrogen flow a deep purple color developed, indicating the presence of vanadium(II) ion. Because the trap could be easily and rapidly regenerated several times by the simple addition of concentrated sulfuric acid, it proved superior to the trap used for initial studies which utilized chromium(II) as an oxygen scavenger. Vanadium(II) was substituted for the chromium(II) oxygen scavenger when it was observed that the latter forms oxidation products which are dissolved with great difficulty and

which therefore interfere with regeneration of the trap.

Preparation of Compounds

Chromium(III) complexes were prepared by methods in the literature. The chromium(III) compounds were analyzed for chromium by the method described in the analytical section.

d-tris(1,10-phenanthroline)chromium(III) perchlorate dihydrate

The method used is identical to that of Hunt et al.[39] In the glove box 0.4 grams of hydrated chromium(II) sulfate (1.7×10^{-3} mole of Cr(II)) was added to a dry three-neck flask equipped with a gas inlet-outlet device, a serum stopper, and a sintered-glass filter device. After removing the assembled flask from the glove box, a stream of nitrogen from the nitrogen train was allowed to flow through the flask for at least 20 minutes to displace the oxygen. A 10 ml. volume of water was added with a hypodermic syringe to dissolve the chromium(II) sulfate, followed by 2.0 g. of 1,10-phenanthroline monohydrate (1.0×10^{-2} mole) dissolved in 20 ml. anhydrous ethanol. Antimony potassium d-tartrate (2.27 g., 6.8×10^{-3} mole) dissolved in 20 ml. of warm water was then added, and a yellow-green precipitate was collected on the filter using nitrogen pressure filtration, washed successively with degassed water and ethanol, and then dispersed in 50 ml. of anhydrous ethanol. Next, 0.60 g. of iodine (4.7×10^{-3} g-atom) dissolved in 30 ml. of ethanol was added as rapidly as possible, while a magnetic stirrer was used to stir the mixture. After several minutes, the alcohol was filtered off, leaving a brown solid. The solid was removed from the reaction flask, treated with 200 ml. of water, and filtered to remove in-

soluble residue. Addition of excess sodium perchlorate to the clear solution precipitated the $Cr(phen)_3^{3+}$ complex as the perchlorate salt. The yellow crystals were filtered and washed with ice-cold water, alcohol, and ether. The product was recrystallized from water and dried in a vacuum desiccator. The specific rotation was found to be +1320 cc./g. dm. when 0.206 g. was dissolved in 100 ml. of water. Analysis: calculated for $Cr(phen)_3(ClO_4)_3 2H_2O$ Cr%=5.61 Found Cr%=5.70.

tris(1,10-phenanthroline)chromium(III) perchlorate dihydrate

obtain. The method used was identical to the one described above except that the addition of antimony potassium d-tartrate was omitted. The visible and near infrared spectra agreed with those reported in the literature. Analysis: calculated for $Cr(phen)_3(ClO_4)_3 \cdot 2H_2O$ Cr%=5.61 Found Cr%=5.70.

Solutions containing the d-tris(1,10-phenanthroline)chromium(III) ion

The perchlorate salt is highly insoluble in water. In order to the necessary concentration of the cation for kinetic studies, an anion exchange resin was used to convert the complex to the more soluble chloride salt. A 10 ml. solution of 0.01 M 1,10-phenanthroline and supporting electrolyte was prepared. A 5 ml. portion of the solution was mixed with a weighted amount of solid $Cr(phen)_3(ClO_4)_3 \cdot 2H_2O$, and an excess of Dowex 2-X8 in the chloride form was added. The mixture was stirred vigorously and then filtered by suction. The remaining 5 ml. of solution was used for two washings leaving only a trace of the yellow complex on the resin. Oxygen was removed from the resulting solution by bubbling purified nitrogen gas through the solution for 20 minutes while stirring with a small magnetic stirring bar. In order to determine the

extinction coefficient of the $Cr(phen)_3^{3+}$ complex, an aliquot of one solution prepared as described above was taken and its spectrum recorded. The chromium content of the solution was analyzed and the extinction coefficient at 525 nm was determined to be 6.8 l./mole cm.

tris(1,10-phenanthroline)chromium(III) Solutions

Solutions containing the racemic cation were prepared by the same procedure as for the optically active ion.

Di-μ-hydroxo-tetrakis(1,10-phenanthroline)dichromium(III) nitrate pentahydrate

The method used was identical to that of Wolcott and Hunt.[63] An aqueous solution 0.1 M in chromium(III) nitrate and 0.4 M in both 1,10-phenanthroline and nitric acid was kept at reflux for 8 hours. Solid sodium hydroxide was added to the solution at the end of the 1, 3, 5, and 7 hours in sufficient quantity to maintain a pH of 4.0. The solution was allowed to cool to room temperature, whereupon violet needles of the nitrate salt precipitated. The filtrate was saved for synthesis of $Cr(phen)_2(H_2O)_2(NO_3)_3 \cdot 5H_2O$. The visible and infrared spectra are in agreement with those reported in the literature. The visible spectrum in 0.1 M nitric acid has a maximum at 535 nm with an extinction coefficient of 48.0 l./mole cm. Analysis: calculated for $(phen)_4Cr_2(OH)_2(NO_3)_4 \cdot 5H_2O$ Cr%=8.77 Found Cr%=8.79. A spectrum of di-μ-hydroxo-tetrakis(1,10-phenanthroline)dichromium ion in 0.01 M phen is shown as spectrum "B" in Figure 1.

diaquobis(1,10-phenanthroline)chromium(III) nitrate

The filtrate from the synthesis of the dimer was acidified to pH 1.0 and refluxed for 3 hours. Upon cooling, orange cyrstals precipitated.

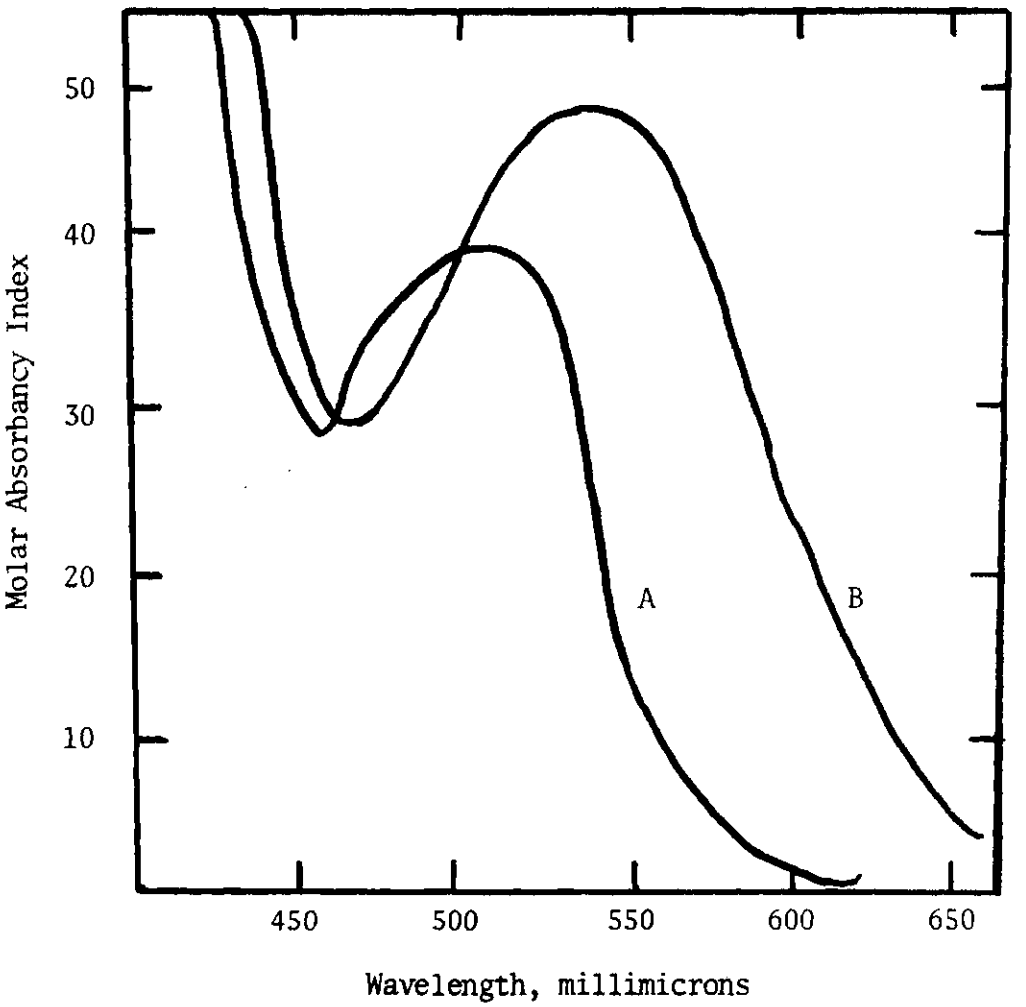


Figure 1. Visible Absorption Spectra of (A) diaquobis(1,10-phenanthroline)chromium(III) nitrate in 0.01 M 1,10-phenanthroline Solution and (B) Di-μ-hydroxo-tetrakis (1,10-phenanthroline)dichromium(III) nitrate in 0.01 M 1,10-phenanthroline Solution.

These were filtered, washed with cold water and air dried. The visible and infrared spectra were in agreement with the report of Inskeep and Bjerrum.[23] A weighted sample was dissolved in 50 ml. of 0.01 M 1,10-phenanthroline solution and its spectrum recorded. An aliquot was taken for chromium analysis and the extinction coefficient at 525 nm was found to be 38.0 l./mole cm. The maximum was 510 nm with an extinction coefficient of 39.2 l./mole cm. Analysis: calculated for $((phen)_2Cr(OH_2)_2)(NO_3)_3$ Cr%=8.23 Found Cr%=8.30. A spectrum of diaquobis(1,10-phenanthroline)chromium(III) ion in 0.01 M phen is shown as spectrum "A" in Figure 1.

chromium(II) sulfate pentahydrate

The compound was prepared by the electrolysis in the cell shown in Fig. 2. In compartment "a" was placed sufficient mercury to cover the platinum electrode. A stir bar was floated on the mercury pool. A solution of 0.1 N in sulfuric acid and 1.0 M in Cr(III) prepared from $Cr_2(SO_4)_3 \cdot nH_2O$ was placed in the 125 ml erlenmeyer flask. The side arm "b" was equipped with a serum stopper. The gas inlet-outlet device was connected to the nitrogen stream. In the middle section "c" was placed 0.1 N sulfuric acid. In secion "d" was placed 0.1 N sulfuric acid and a platinum spiral electrode. The solution was flushed with nitrogen prior to electrolysis and electrolyzed at a current of 0.10 amperes for 26 hours with a variable DC power supply. As the electrolysis proceeded, blue crystals of the products began to crystalize. At the completion of the electrolysis the mercury was poured off by opening stopcock "e". The solid product was gathered on frit "f", and washed with 10 ml. of oxygen free water, injected through the serum stopped. The cell was trans-

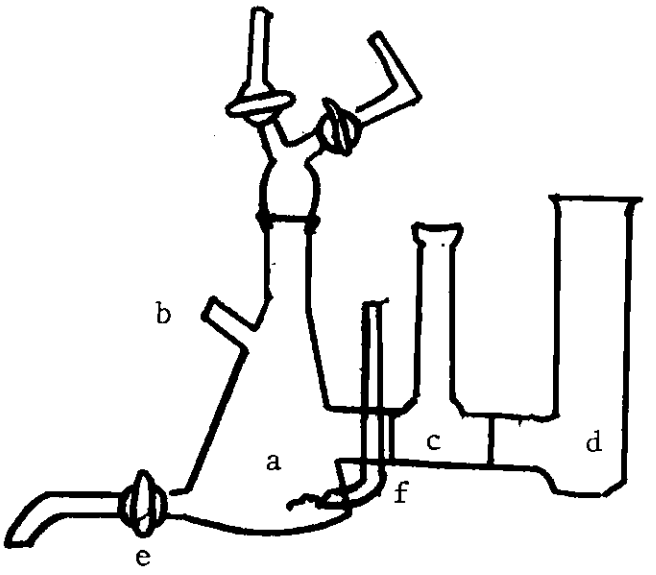


Figure 2. Electrolysis Cell

ferred to the glove box and the chromium(II) sulfate removed and placed in a desiccator. The Cr(II) is stable when stored in the glove box but the salt gradually dehydrates, changing from blue $CrSO_4 \cdot 5H_2O$ to the white anhydrous salt.

tris(1,10-phenanthroline)chromium(II) ion formed in situ

The ion was formed under different conditions depending upon the experiment.

(1) For measuring the rate of hydrolysis and the rate of the loss of optical activity, the complex was prepared in the same fashion. In the glove box, approximately 0.1 g. of chromium(II) sulfate was dissolved in 50 ml. of water. Approximately 0.05 ml. of the chromium(II) sulfate solution was withdrawn into a 5 ml. syringe with a 2 inch teflon needle. The needle of the syringe was placed in a solution containing the supporting electrolyte and 0.01 M 1,10-phenanthroline. Approximately 4 ml. of the phen solution was drawn up into the syringe containing the chromium(II) sulfate solution, resulting in the formation of the olive-green tris(1,10-phenanthroline)chromium(II) ion in the syringe. The reaction cell, capacity approximately 3 ml., was filled beyond the mark with the $Cr(phen)_3^{2+}$ solution and the remaining solution in the syringe was discarded. The Cr(II) concentration was estimated by the intensity of the olive-green color. The solution in the reaction cell was drawn back into the 5 ml. syringe and, if needed, the concentration was adjusted by adding either more phenanthroline or chromium(II) solution. The solution was transferred back and forth between the cell and the syringe at least twice to insure proper mixing.

(2) For the dissociation kinetics of tris(1,10-phenanthroline)

chromium(II) ion, a different technique was used. In the glove box 0.4 g. of chromium(II) sulfate was dissolved in 25 ml. of water and placed in a 50 ml. erlenmeyer flask. The flask was sealed with a serum stopper and removed from the glove box.

In the reservoir of a 25 ml. automatic buret, shown in Fig. 3, was placed 150 ml. of 0.01 M 1,10-phenanthroline solution. The reservoir stopper was sealed with wax. The bulb was placed in a dry ice-acetone bath and frozen. The tip of the buret was connected to a vacuum line and the system was evacuated. After the pressure was lowered, stopcock "a" was turned to isolate the buret from the pump. Stopcock "b" was kept open during all operations. The solution was thawed and trapped gas was evolved from the solution. The solution was frozen again and evacuated to remove the gas released when the solution was thawed. The cycle was repeated three times. The connection to the vacuum line was removed and a one-inch stainless steel needle was connected to the buret. The needle was inserted into the 50 ml. erlenmeyer flask containing the chromium(II) sulfate solution. The flask was also connected to the nitrogen stream by inserting a needle from the nitrogen stream as well as a needle to serve as a gas exit. Stopcock "a" was opened slightly and the chromium(II) solution was sucked into the graduated part of the buret. Stopcock "a" was closed and the solutions were mixed. If necessary, more chromium(II) solution was added to give the approximate concentration desired that was estimated visibly. The reservoir and buret were then pressurized to 2 atmospheres and 1 atmosphere respectively by the following procedure. The stainless steel needle was removed and the tip of the buret connected to the nitrogen

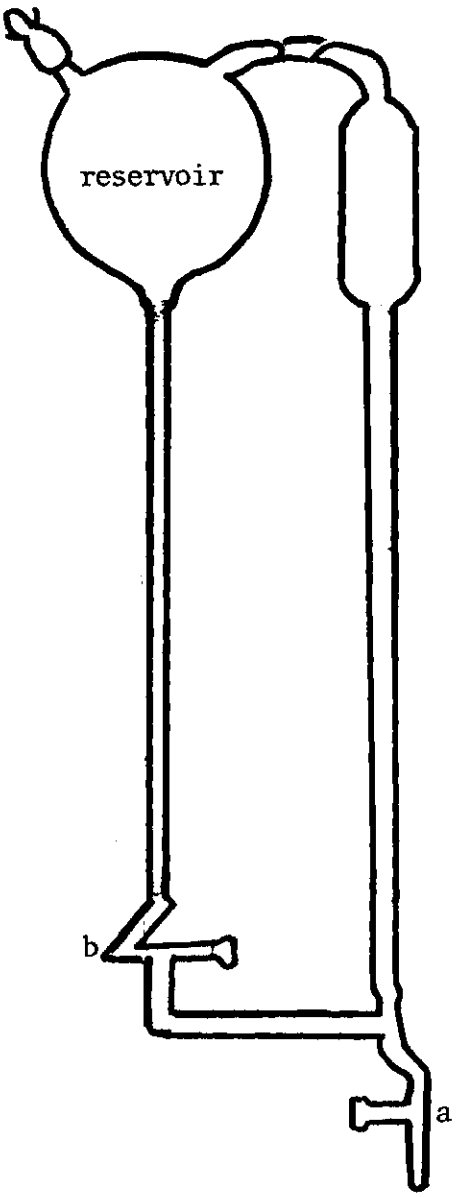


Figure 3. Sealed Automatic Buret

stream with tygon tubing. By inverting the apparatus and opening stopcocks "a" and "b", the apparatus was pressurized with purified nitrogen to about 2 atmospheres. The stopcocks were closed. The apparatus was tilted back to an upright position and the tip was immersed slightly in a pool of mercury. The pressure in the buret was reduced to 1 atmosphere by opening stopcock "a" only for the time needed to release the excess nitrogen gas.

Chromium(III) Analysis in the Presence of 1,10-phenanthroline

An attempt was made to analyze for chromium by dissolving the chromium(III) phenanthroline complex in water, making the system basic with sodium hydroxide, and oxidizing the chromium(III) to chromium(VI) with hydrogen peroxide. The hydrogen peroxide was destroyed by boiling. When the spectrum was recorded, a new absorbance peak was observed at 325 nm. The new peak was not removed by boiling the sample for an hour. On a known Cr(VI) and 1,10-phenanthroline sample, the new peak changed the absorbance of the chromate peak at 368 nm from 0.300 to 0.310. The change in absorbance proved to be a function of the chromate concentration, the length of time the solution was boiled, and the degree of evaporation prior to dilution to volume.

Prior extraction of any excess 1,10-phenanthroline with chloroform, followed by oxidation in base with hydrogen peroxide, still produced the new peak at 325 nm. Extraction of the chromate solution after oxidation did not remove the interference at 325 nm but did remove some of the chromium(VI).

An attempt was made to use ammonium persulfate as oxidant in the presence of silver (I) ion as catalyst. Following the procedure as de-

scribed for steel samples,[65] the results were erratic but generally low when chloride or perchlorate were present. The procedure was abandoned without detailed investigation of the erratic results. It is believed that volatile chromyl chloride was formed, explaining the generally low results.

In order to avoid the above problems, the following procedure was adopted from the analysis of chromium in blood.[66] The sample was decomposed with nitric acid and hydrogen peroxide with heat to insure that the chromium remained in the plus three oxidation state. To a weighed solid sample or an aliquot was added 3 ml. of concentrated nitric acid and the mixture was carefully evaporated to dryness on a hot plate. The sample was not allowed to bake. This was done two more times. The dried sample was taken up with two or three drops of concentrated nitric acid and 40 ml. of 2 M KOH was added. A 2 ml. volume of potassium hypochlorite solution was added. The hypochlorite was formed by passing chlorine gas through 2 M KOH solution. After the addition of hypochlorite, the solution was allowed to slowly evaporate on a hot plate until potassium hydroxide began to crystalize. The solution was diluted to approximately 40 ml with water, then diluted to mark in a volumetric flask with 2 M KOH. The absorbance was read at 368 nm on a Cary Model 16 spectrophotometer. The chromium concentration was calculated from a standard curve. An extinction coefficient of 4784 l./mole cm. at 368 nm (the maximum as measured on the Cary 16 and 14 spectrophotometer) for chromate agrees within 0.6% of the value for the maximum reported by Haupt.[67]

Determination of the Extinction Coefficient of $Cr(phen)_3^{2+}$

The spectrum of $Cr(phen)_3^{2+}$ was recorded on a Cary Model 14 spectrophotometer from 400 nm to 1200 nm and agreed with the report in the literature.[46] Visible absorption maxima were observed at 480 nm and 810 nm. The extinction coefficient was evaluated at 480 nm.

A completely sealed system was employed because the high extinction coefficient made dilute solutions necessary. This in turn made oxidation a real problem, so that it was necessary to analyze for Cr(II) in the solution whose spectrum was measured. The flask shown in Figure 4 was used. In tip tube "a" was placed solid ferric chloride. The tip of the stopcock "b" was connected to a vacuum line. In the bottom of the flask was placed 100 ml of 0.01 M 1,10-phenanthroline and a break bulb containing chromium(II) sulfate. The bulb was prepared as described in the literature.[68] The break bulb breaker, "c", was filled with iron shot and a magnetic stir bar and sealed. The flask was sealed with wax. The break bulb breaker was held suspended during the following operations with an external magnet. The solution was frozen in a dry ice-acetone bath and stopcock "b" was opened permitting the system to be evacuated. The stopcock was closed and the solution thawed. The thawed solution released trapped gas to the vacuum. The solution was frozen and evacuated again. The cycle was performed three times. With stopcock "b" closed and the solution thawed, the vacuum line connection was removed. The break bulb was broken by removing the external magnet, allowing the breaker to drop and crush the break bulb. The $Cr(phen)_3^{2+}$ complex was formed on mixing the reactants and absorption at 480 nm was initially measured. A small initial decrease in the ab-

sorbance was generally observed, probably due to reaction of oxygen absorbed on the walls. Because of the low absorbance at 480 nm of the oxidation product, $Cr(phen)_2(H_2O)_2^{3+}$, the error due to this source was considered negligible. When the absorption no longer changed with time, the absorption was recorded, the flask was inverted and the chromium(II) was oxidized by the iron(III) contained in "a". This operation was performed as quickly as possible. The absorption of $Fe(phen)_3^{2+}$ at 510 nm was read in the 0.15 cm. cell, "e". The absorption of $Fe(phen)_3^{2+}$ was corrected by measuring the absorbance of a blank of solid ferric chloride dissolved in 0.01 M 1,10-phenanthroline. The concentration of $Fe(phen)_3^{2+}$ was calculated from a standard curve, determined in 0.01 M 1,10-phenanthroline solution. The $Cr(phen)_2(H_2O)_2^{3+}$ formed by the oxidation of $Cr(phen)_3^{2+}$ does not absorb appreciably at 510 nm. The $Cr(phen)_3^{2+}$ was corrected for a blank of 0.01 M 1,10-phenanthroline. The spectrum of $Cr(phen)_3^{2+}$ is shown in Figure 5.

Four successive runs gave molar extinction coefficients of 3.19, 3.16, 3.21, and 3.19×10^3 1./mole cm. at 480 nm. The average value of 3.19×10^3 1./mole cm. is used in further calculations. The reproducibility was $\pm$ 1%. The variation of the absorption of $Cr(phen)_3^{2+}$ with concentration over an absorbance range of 0.4 to 1.2 proved a valid application of the Beer-Lambert Law.

Kinetic Studies

Kinetics of the Acid Dissociation of tris(1,10-phenanthroline)chromium(II) ion

A sealed automatic buret, described in the previous section, con-

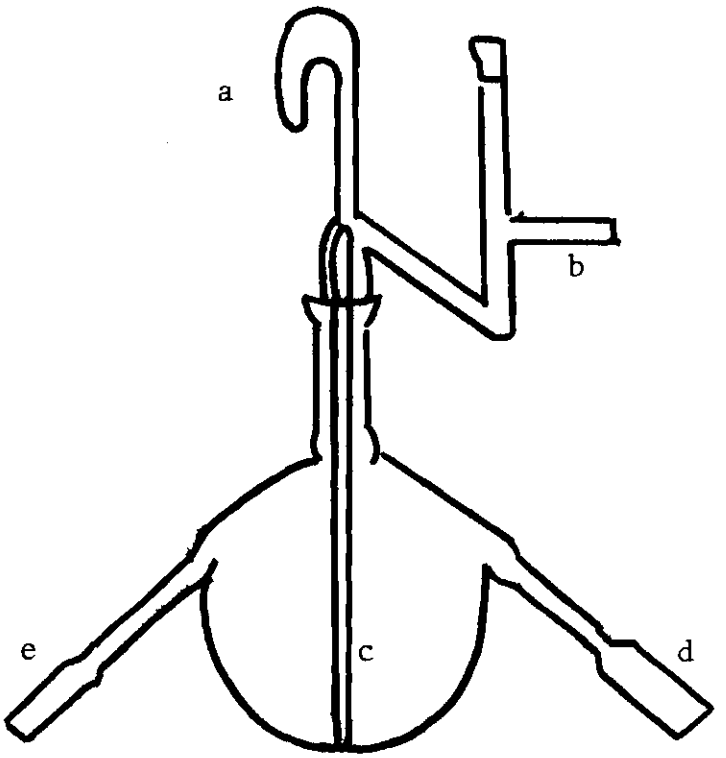


Figure 4. Sealed Flask

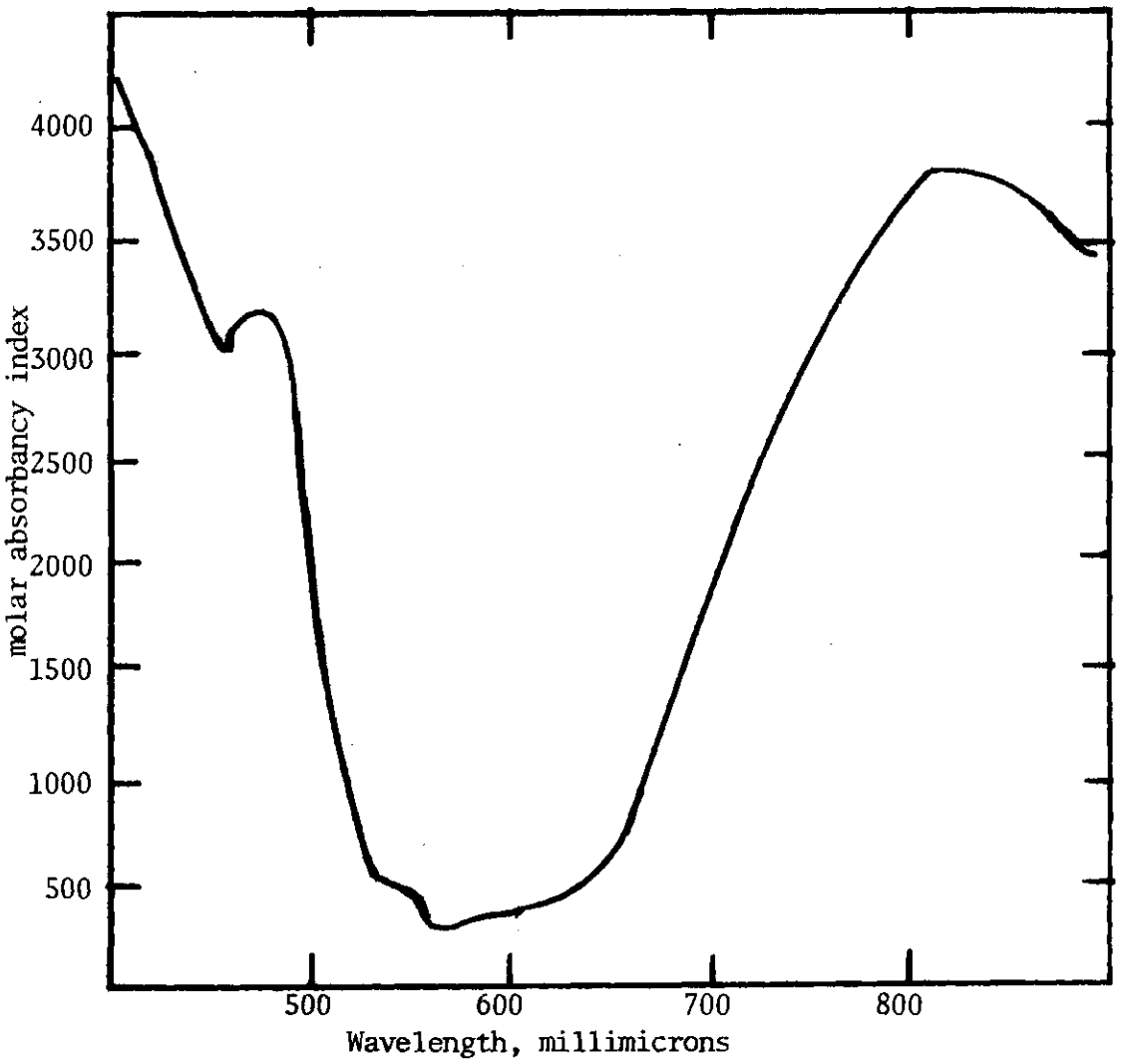


Figure 5. Visible Absorption Spectrum of Tris(1,10-phenanthroline) chromium(II)

taining $Cr(phen)_3^{2+}$ and 0.01 M 1,10-phenanthroline, was equipped with a syringe needle. A 1 cm. cell with a serum stopper was flushed with nitrogen. The 1 cm. cell was partially filled with about 3 cc. of the solution from the buret, while the nitrogen stream was maintained. The cell was placed in a Cary Model 14 spectrophotometer. The absorbance of the $Cr(phen)_3^{2+}$ complex was measured. One-half ml of 6.0 M HCl was injected into the cell and the contents mixed manually as quickly as possible. The absorbance at 480 nm was recorded as a function of time.

Kinetics of the Hydrolysis of $Cr(phen)_3^{3+}$ as catalyzed by $Cr(phen)_3^{2+}$

A 3 cm. fused quartz polarimeter cell as shown in Figure 6 was purchased from Bendix Corporation. The cell was taken into the glove box. $Cr(phen)_3^{2+}$, as described in the previous section, was placed in the path length section of the cell and filled to the mark. The cell volume had been previously determined by weighing with water to the mark. An aliquot of $Cr(phen)_3^{3+}$ solution was placed in the tip tube bulb. The tip tube was greased with silicone grease and connected to the body of the cell. The cell was removed from the glove box and placed in the Cary Model 16 spectrophotometer. Masks of black painted aluminum metal were fabricated to collimate the light beam to a diameter slightly less than that of the cell face. These masks were placed in front of the cell face and in the reference beam.

The absorbance of $Cr(phen)_3^{2+}$ at 480 nm was read as a function of time in order to check the rate of oxidation of $Cr(phen)_3^{2+}$. If the rate of oxidation of $Cr(phen)_3^{2+}$ was greater than 3×10^{-7} mole/l. min., the solution was discarded. A blank was measured at 480 nm with water in the cell and the masks in place. The cell was connected to a water bath by

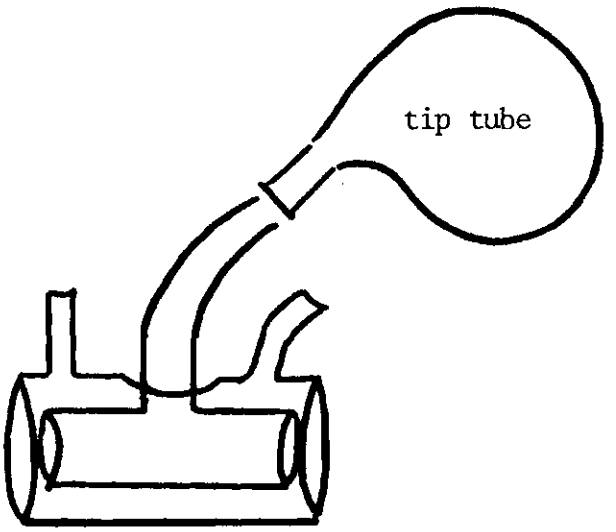


Figure 6. Fused Quartz Polarimeter Cell.

the connecting hoses to the water jacket. The water was circulated for 10 minutes when the cell was near room temperature. When the water bath temperature was greater than room temperature by 5 degrees, the water was circulated for 20 minutes. The contents were mixed and the absorbance at 525 nm was recorded as a function of time using a Cary Model 14 spectrophotometer.

Kinetics of the Loss of Optical Activity of d-$Cr(phen)_3^{3+}$ as Catalyzed by $Cr(phen)_3^{2+}$

The same cell, Figure 6, that was used in the hydrolysis study was used in the study of the loss of optical activity. The cell with the d-$Cr(phen)_3^{3+}$ and $Cr(phen)_3^{2+}$ solutions were prepared in the same fashion as for the hydrolysis. Similarly the oxidation was checked at 480 nm in a Cary Model 16 spectrophotometer. If the rate of oxidation of $Cr(phen)_3^{2+}$ was greater than 3×10^{-7} mole/l. min., the solution was discarded. The cell was removed from the spectrophotometer and connected to the water bath. The cell was equilibrated as described for the hydrolysis. The contents of the tip tube and the cell body were mixed by tilting the cell upside down so that the $Cr(phen)_3^{2+}$ entered the tip tube. This was done twice to ensure total mixing. It took approximately 30 seconds to mix the contents and place the cell in the polarimeter. The change of the rotation with time of the solution was measured with a Bendix Ericsson automatic polarimeter with an ETL NPL type 143A optical unit and a Texas Instrument Company Model FWS strip chart recorder using an interference filter for the 546 nm Hg lines. The average uncertainty of a reading on the $\pm$0.5 degree scale was $\pm$ 1%; and on the $\pm$.-1 degree scale, was $\pm$ 2%. When the reaction had proceeded

more than 6 half lives, the cell was removed from the polarimeter and placed in the spectrophotometer. Absorbance at 480 nm was measured to check if the $Cr(phen)_3^{2+}$ had been oxidized. The cell was replaced in the polarimeter and the infinite reading was taken. The infinite reading agreed with a blank reading of water in the cell.

The pH of the reaction mixture was determined with a Beckman Research pH meter. When desired, the pH was changed by the addition of HCl to the 1,10-phenanthroline solution. The solution appeared to be acceptably buffered by the excess 1,10-phenanthroline. No other buffers were used, to avoid possible interference by the buffer in the electron transfer reaction.

It should be noted that the reaction cell should NOT be cleaned in chromic acid solution. Chromium(VI) is retained on the cell walls and causes appreciable oxidation of chromium(II) when the reactants are mixed. The cell was cleaned in a 1:1 boiling mixture of nitric acid and hydrochloric acid.

Analysis of Reaction Products

Dissociation Reaction

The spectrum of the products of the reaction of $Cr(phen)_3^{2+}$ with HCl was recorded. The spectrum showed no absorbance in the visible region except that of 1,10-phenanthroline. Using an extinction coefficient of 45 l./mole cm. for 1,10-phenanthroline at 480 nm, the infinite absorbance reading corresponded to that of a 0.01 M 1,10-phenanthroline solution alone. It is assumed that the rate determining step is the dissociation of the first 1,10-phenanthroline molecule.

Hydrolysis Reaction

The reaction products of the hydrolysis of $Cr(phen)_3^{3+}$ were expected to be either the monomeric $Cr(phen)_2(H_2O)_2^{3+}$ or the dimer $((phen)_2Cr(OH)_2Cr(phen)_2)^{4+}$. These ions were synthesized as described previously. A Dowex 50W-4X cation exchange column, 1 cm. in diameter by 20 cm. in height, was equilibrated with 3 M HCl, then washed thoroughly with water. All three ions were placed on the column. $Cr(phen)_3^{3+}$ was eluted with 3.6 M HNO_3 from the column. Separation of the monomer from the dimer was found to be possible using 5.3 M HNO_3 as an eluant. The bands are broad and tend to overlap. $HClO_4$ and La(III) were tried as eluants but gave poor results.

Reaction products from the hydrolysis were placed on the column, after quenching the reaction with rapid air oxidation of $Cr(phen)_3^{2+}$. The column was eluted with 3.6 M HNO_3 to remove the $Cr(phen)_3^{3+}$ ion. When the column was eluted with 5.3 M HNO_3, the monomer was the only reaction product identified spectrophotometrically in the eluate, regardless of the extent of the reaction. The nitric acid concentration was increased to 8.0 M and no dimer was observed.

To test the conclusion that the only product was the monomer, a hydrolysis reaction was performed with the monomer substituted for the $Cr(phen)_3^{3+}$. No change in the absorbance with time at 525 nm was observed after mixing.

CHAPTER III

RESULTS

Dissociation Reaction

The dissociation reaction was followed by measuring the rate of decrease of the absorbance of $Cr(phen)_3^{2+}$ at 480 nm. The rate law was found to be

$$\frac{d[\ Cr(phen)_3^{2+}]}{dt} = -k_1[\ Cr(phen)_3^{2+}] \qquad (9)$$

where k_1 is a first order rate constant for the reaction

$$Cr(phen)_3^{2+} + H^+ \longrightarrow Cr(phen)_2^{2+} + phenH^+ \qquad (10)$$

Integrating Equation 9 gives

$$-\ln \frac{[Cr(phen)_3^{2+}]_t}{[Cr(phen)_3^{2+}]_i} = k_1 t \qquad (11)$$

where "i" refers to time = 0 and "t" refers to time from mixing time. As shown in Appendix 1, Equation 11 can be written as

$$\ln(A_t - A_\infty) - \ln(A_i - A_\infty) = -k_1 t \qquad (12)$$

Since $\ln(A_i - A_\infty)$ for a given experiment is a constant, the plot of $\ln(A_t - A_\infty)$ versus time should give a linear plot with a slope of $-k_1$, and an intercept of $\ln(A_i - A_\infty)$. A typical plot of $\ln(A_t - A_\infty)$ versus time is shown in Figure 7. The plot was linear for four half lives. In a series of experiments, k_1 was calculated from the slope to give the following values: 0.073, 0.091, 0.089, 0.086, 0.080, and 0.082 $sec.^{-1}$. The average value is 0.083 $sec.^{-1}$. The relatively large spread can be attributed to the use of conventional spectroscopic techniques for a reaction with a half life of approximately 9 seconds. The slope used to calculate k_1 was taken from the best visual line.

Hydrolysis Reaction

The mechanism proposed for the hydrolysis of $Cr(phen)_3^{3+}$ as catalyzed by $Cr(phen)_3^{2+}$ is:

$$CrL_3^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CrL_2^{2+} + L \qquad (13)$$

$$CrL_3^{3+} + CrL_2^{2+} \xrightarrow{k_3} CrL_3^{2+} + CrL_2^{3+} \qquad (14)$$

where the water molecules have been omitted for convenience and L = 1,10-phenanthroline. Assuming a steady state concentration of CrL_2^{2+}, the rate as expressed in terms of the increase of CrL_2^{3+}, can be written as:

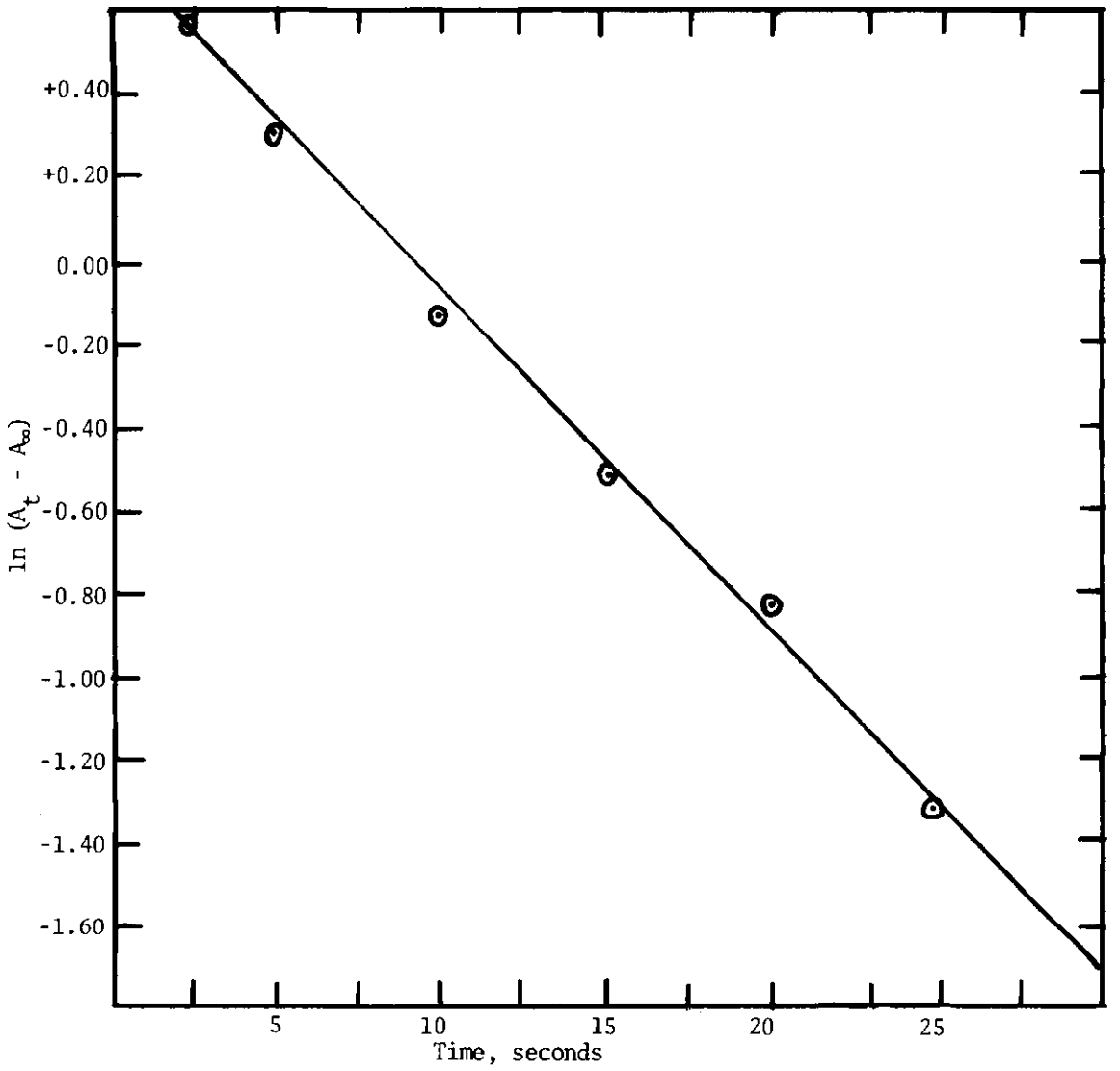


Figure 7. Typical Plot of ln (A_t - A_∞) Versus Time

$$\frac{d\,[CrL_2^{3+}]}{dt} = \frac{k_3 k_1\,[CrL_3^{2+}]\,[CrL_3^{3+}]}{k_2[L] + k_3\,[CrL_3^{3+}]} \tag{15}$$

if $k_3[CrL_3^{3+}]$ is much greater than $k_2[L]$, then Equation 15 becomes:

$$\frac{d\,[CrL_2^{3+}]}{dt} = k_1[CrL_3^{2+}] \tag{16}$$

Integrating Eq. 16 gives:

$$[CrL_2^{3+}]_t - [CrL_2^{3+}]_i = k_1[CrL_3^{2+}]t \tag{17}$$

where "t" refers to time "t" and "i" refers to the initial time and $[CrL_3^{2+}]$ is assumed to remain constant. At time equal zero, the initial concentration of CrL_2^{3+} is equal to zero. $[CrL_2^{3+}]_t$ can easily be shown to be related to the adsorbance at time "t" by the following expression:

$$[CrL_2^{3+}]_t = \frac{A_t}{b(e'' - e')} + C \tag{18}$$

where:

A_t = absorbance at time "t"

b = path length of spectrophotometer cell

$$c = -\frac{e[CrL_3^{2+}]}{e'' - e'} - \frac{e'[CrL_3^{3+}]_i}{e'' - e'}$$

e'' = extinction coefficient of CrL_2^{3+} at 525 nm

e' = extinction coefficient of CrL_3^{3+} at 525 nm

e = extinction coefficient of CrL_3^{2+} at 525 nm

Substituting Equation (18) into Equation (17) yields:

$$\frac{A_t}{b(e'' - e')} + C - (CrL_2^{3+})_i = k_1(CrL_3^{2+})t \qquad (19)$$

A plot of A_t versus time should be linear. The slope of such a plot would be equal to $k_1(CrL_3^{2+})b(e'' - e')$ from which the rate constant k_1 can be calculated. A typical plot of A_t versus time is shown in Figure 8. The curvature of the plot could be due to the slow oxidation of chromium(II) or to the breakdown of the approximation that $k_2(CrL_3^{3+})$ is much greater than $k_2(L)$. Certainly the approximation becomes less good as the reaction proceeds. Despite the curvature, the constancy of k_1 over a five-fold variation in the Cr(III) concentration and a three-fold variation in the Cr(II) concentration supports the reaction orders of 1 and 0 for Cr(II) and Cr(III) respectively. Attempts were made to calculate k_2 and k_3 by applying the data to Equation 15; however, the data were not of sufficient accuracy to give reliable results. From Equation 15 it appears that different limiting rate laws might be observed at low and high phenanthroline concentrations. This effect was tested by varying the phenanthroline concentration over a small range limited by the low solubility of 1,10-phenanthroline in water and on the other hand by the need for sufficient ligand concentration to insure that Cr(II) will be present as $Cr(phen)_3^{2+}$. The results of these experiments and those in which KCl was added are shown in Table 3.

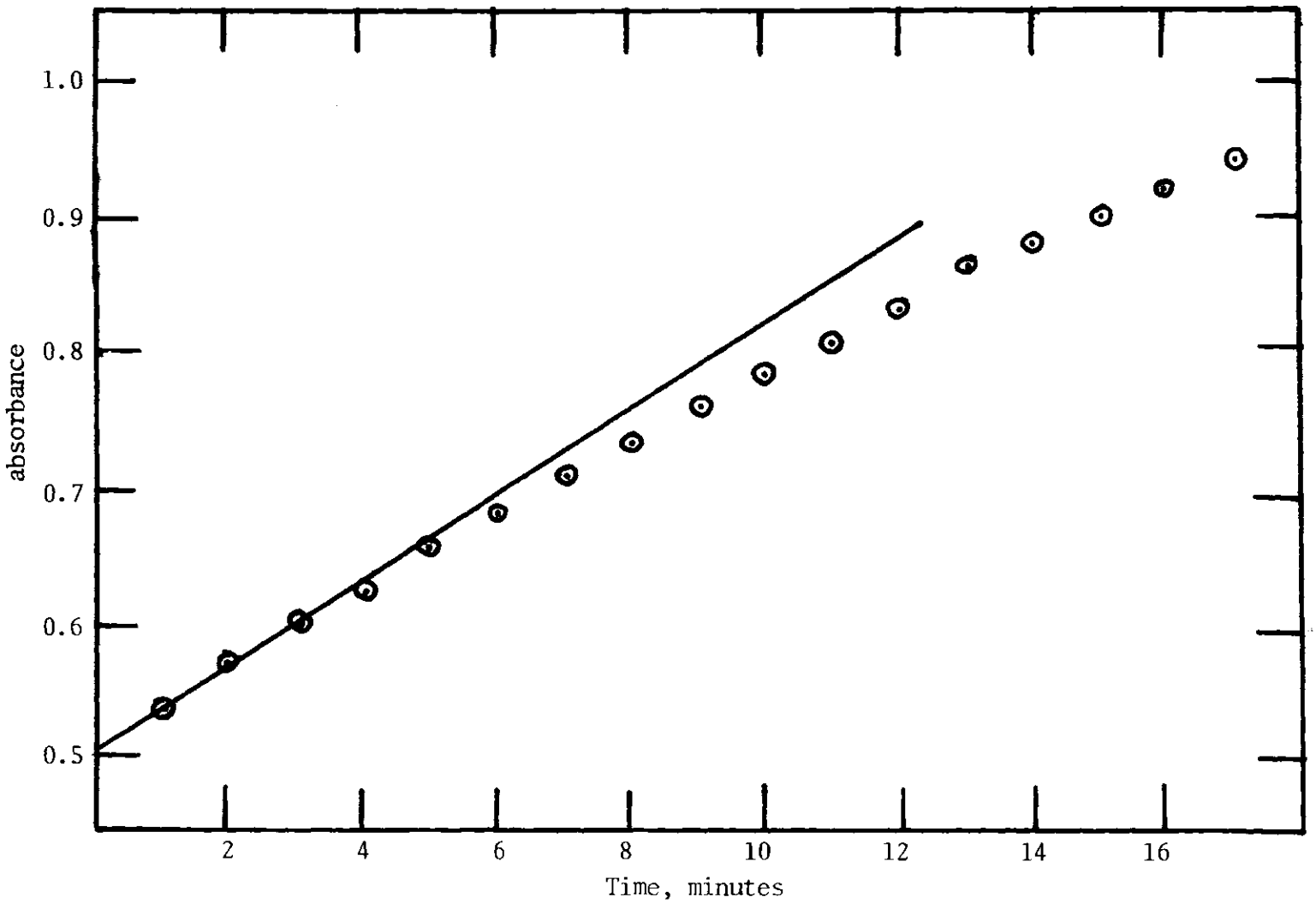


Figure 8. A Typical Plot of Absorbance Versus Time for the Hydrolysis

Table 3. Rate of Hydrolysis of $Cr(phen)_3^{3+}$ as Catalyzed by $Cr(phen)_3^{2+}$ at 26.5°

Run Number	$Cr(phen)_3^{2+}$ x 10^5 M	$Cr(phen)_3^{3+}$ x 10^3 M	Medium	k_1 $Sec.^{-1}$
1	8.18	5.40	0.01M KCl, 0.01M phen	0.078
2	5.28	9.26	0.01M KCl, 0.01M phen	0.081
3	6.35	9.26	0.01M KCl, 0.01M phen	0.090
4	6.64	6.24	0.01M phen	0.079
5	9.11	10.71	0.01M phen	0.083
6	14.81	3.40	0.009M phen	0.085
7	8.02	2.12	0.009M phen	0.076
8	6.10	6.24	0.0083M phen	0.088
9	9.75	10.5	0.006M phen	0.085
10	6.52	10.5	0.006M phen	0.090
11	5.99	6.24	0.0017M phen	0.077
12	11.0	6.24	0.0017M phen	0.084

Average 0.083 ± 0.007

A series of reaction was conducted with temperature being the variable so that the activation energy could be determined. The activation energy, E_a, is given by the conventional relation:

$$k = Ae^{-E_a/RT} \tag{20}$$

A plot of ln k_1 versus 1/T should be linear and the slope is equal to $-E_a/R$. The data are contained in Table 4 and plotted in Figure 9.

According to the transition-state theory of chemical kinetics, the specific rate constant is given by:

$$k = (k'RT/Nh)e^{\Delta S/R} e^{-\Delta H/RT} \tag{21}$$

where:

k' = the transmission coefficient

R = gas constant

N = Avogadro's number

h = Planck's constant

ΔS = entropy of activation

ΔH = enthalpy of activation

It is generally assumed (1) that the variation of the preexponential term with temperature is small, (2) that k' = 1, and (3) that the enthalpy of activation is approximately equal to the activation energy. The activation energy was found to be 21.3 Kcal./mole and the entropy of activation was found to be 7 cal./deg.mole.

Table 4. Rate of Hydrolysis at Various Temperatures in 0.01M 1,10-phenanthroline

Number of Samples	Temperature C°	Reciprocal of Temperature $°K^{-1} \times 10^3$	k_1 sec^{-1}	$\ln k_1$
3	36.0	3.234	0.226	-1.487
6	31.1	3.286	0.126	-2.071
6	26.5	3.337	0.0835	-2.489
4	18.0	3.434	0.234	-3.755

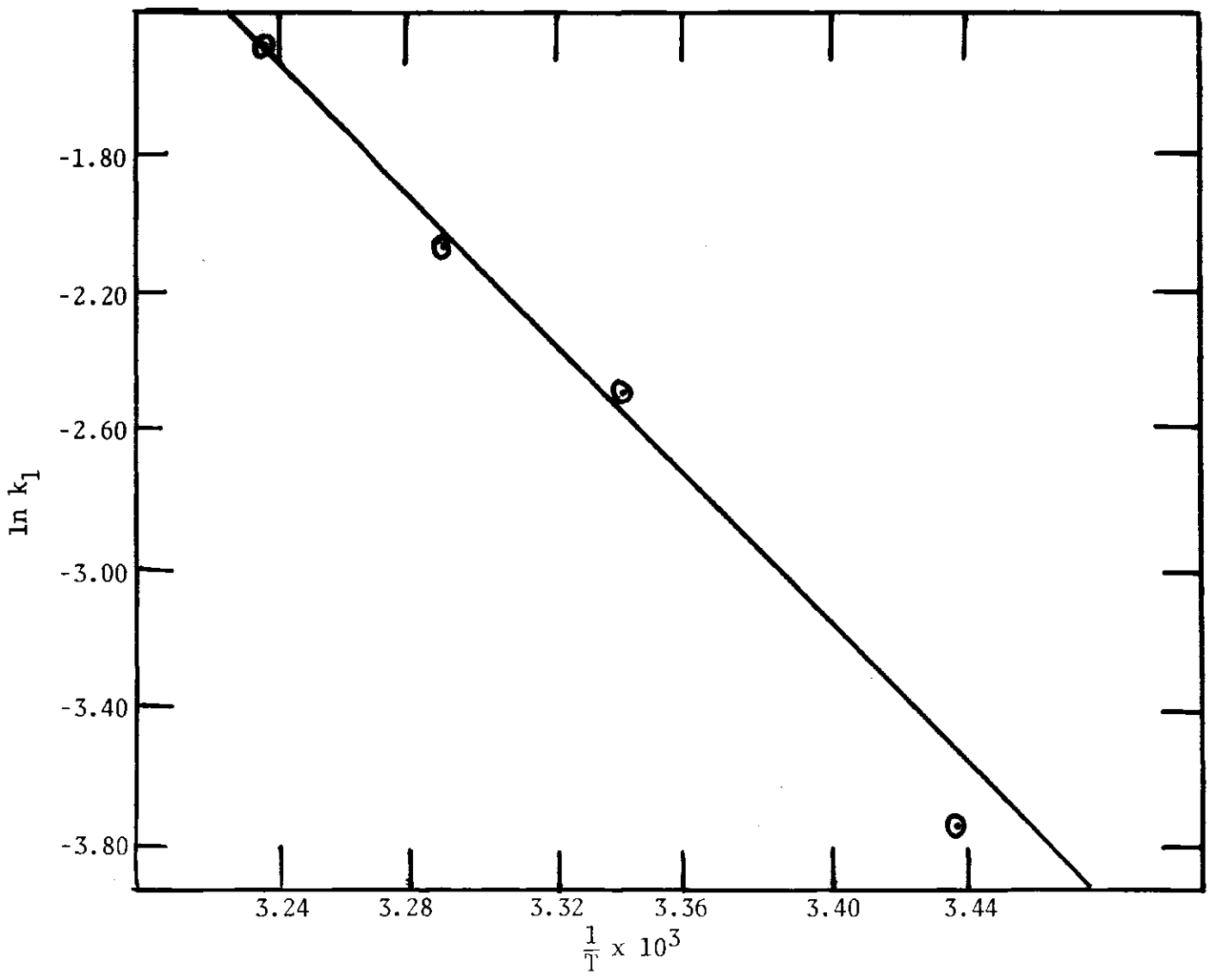


Figure 9. Activation Energy of the Hydrolysis Reaction

Loss of Optical Activity

If the hydrolysis reaction is the only reaction taking place, then Equation 8 can be written in terms of CrL_3^{3+} instead of CrL_2^{3+} as:

$$[CrL_3^{3+}]_t - [CrL_3^{3+}]_i = -k_1[CrL_3^{2+}]_t \qquad (22)$$

If only one optical isomer is present* then the concentration of the isomer is directly proporational to the angle of rotation α . Equation 13 becomes:

$$c\alpha_t - c\alpha_i = -k_1[CrL_3^{2+}]t \qquad (23)$$

where c is the proportionality constant. A value of 472 degree l./mole was calculated for c from the specific rotation. A linear relationship is thus predicted between α_t and t. Figure 10 shows that a plot of $(\alpha_t - \alpha_i)$ versus t using typical data is not linear. Furthermore, the rate of change of rotation with time is faster than can be accounted for by hydrolysis alone. Using the linear approximation between the first data point and the intercept gives a first-order constant approximately 2.5 times as large as k_1 measured in the hydrolysis studies. This result suggests loss of optical activity is proceeding by two pathways.

A possible parallel path involves an exchange reaction such as that tested experimentally by Im and Busch. These authors have derived the following formula for the change of rotation with time when one of

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*If both optical isomers are present, it can be easily shown that a linear relationship is still predicted.

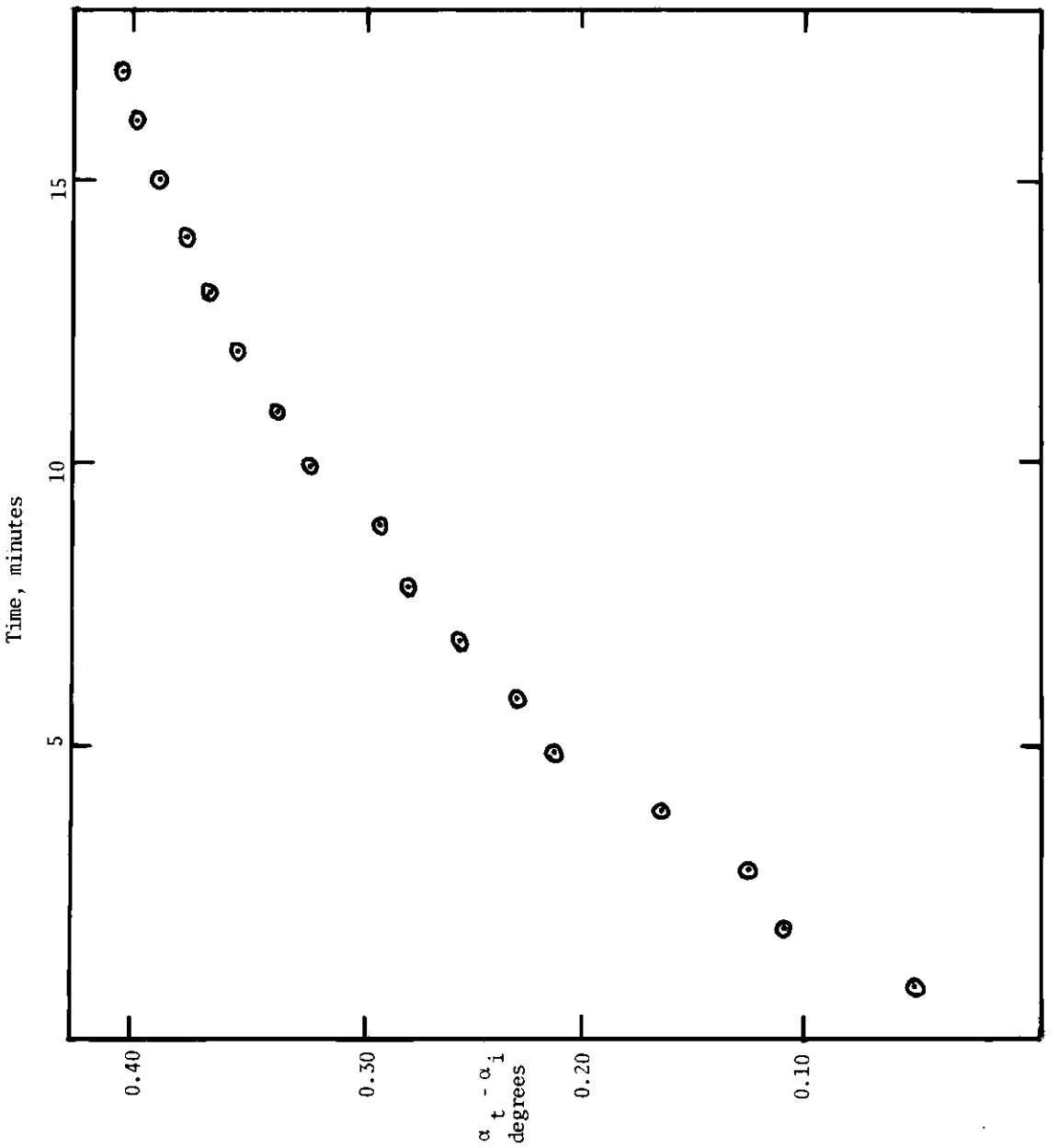

Figure 10. A Linear Plot of Rotation Versus Time

the reactants in configurationally unstable:

$$-\ln\alpha_t + \ln\alpha_i = Rt/[CrL_3^{3+}] \qquad (24)$$

where R = equilibrium constant of the rate of exchange. A typical plot of $\ln\alpha_t$ versus time is shown in Figure 11. The initial slope is observed to be well defined from such plots. The observed curvature is attributed to the hydrolysis of CrL_3^{3+} that was assumed to be constant in Equation 24.

Order of the Reaction

The exchange rate, R, can be expressed as *

$$R = k_e[CrL_3^{2+}]^m[CrL_3^{3+}]^n \qquad (25)$$

Substituting Equation 25 into Equation 24 yields

$$-\ln\alpha_t + \ln\alpha_i = k_e[CrL_3^{2+}]^m[CrL_3^{3+}]^{n-1}t \qquad (26)$$

If CrL_3^{3+} is kept constant, and if one obtains the initial slope from a $\ln\alpha_t$ versus time plot, then m can be determined from the slope of a $\ln -(\text{slope})_i$ versus $\ln[CrL_3^{2+}]$ plot. Table 5 shows the data points plotted in Figure 12. The slope is equal to 1.01 and therefore m is equal to one.

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*The following discussion assumes that the exchange reaction is the only reaction taking place. It is known that the hydrolysis reaction is also taking place. For the case in which the exchange reaction rate order is different from the hydrolysis order, the value of the order found will be expected to be fractional.

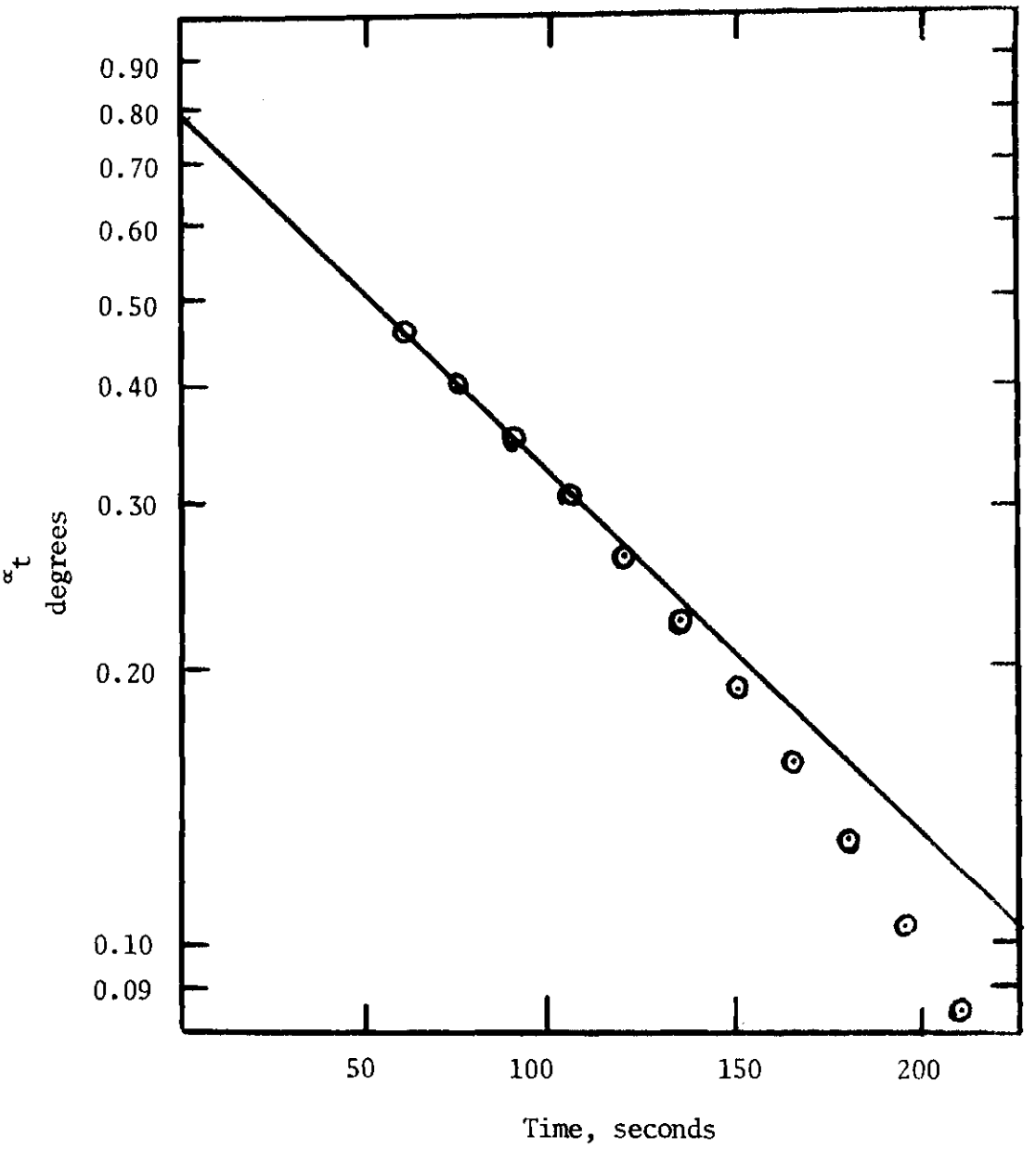

Figure 11. Typical Plot of Rotation Versus Time

Table 5. Order of the Loss of Optical Activity with Respect to $Cr(phen)_3^{2+}$ Ion. In 0.0094 M 1,10-phenanthroline, at 25.8°C, with a constant $Cr(phen)_3^{3+}$ of 1.97×10^{-3} M.

Number	$Cr(phen)_3^{2+}$ $\times 10^5$ M	ln $Cr(phen)_3^{2+}$	$-(slope)_i$ $\times 10^3$	ln $-(slope)_i$
1	5.37	-9.832	5.99	-5.117
2	6.71	-9.609	6.78	-4.994
3	8.67	-9.353	9.37	-4.670
4	7.60	-9.485	8.22	-4.801
5	4.56	-9.996	4.99	-5.300
6	14.36	-8.848	15.65	-4.157

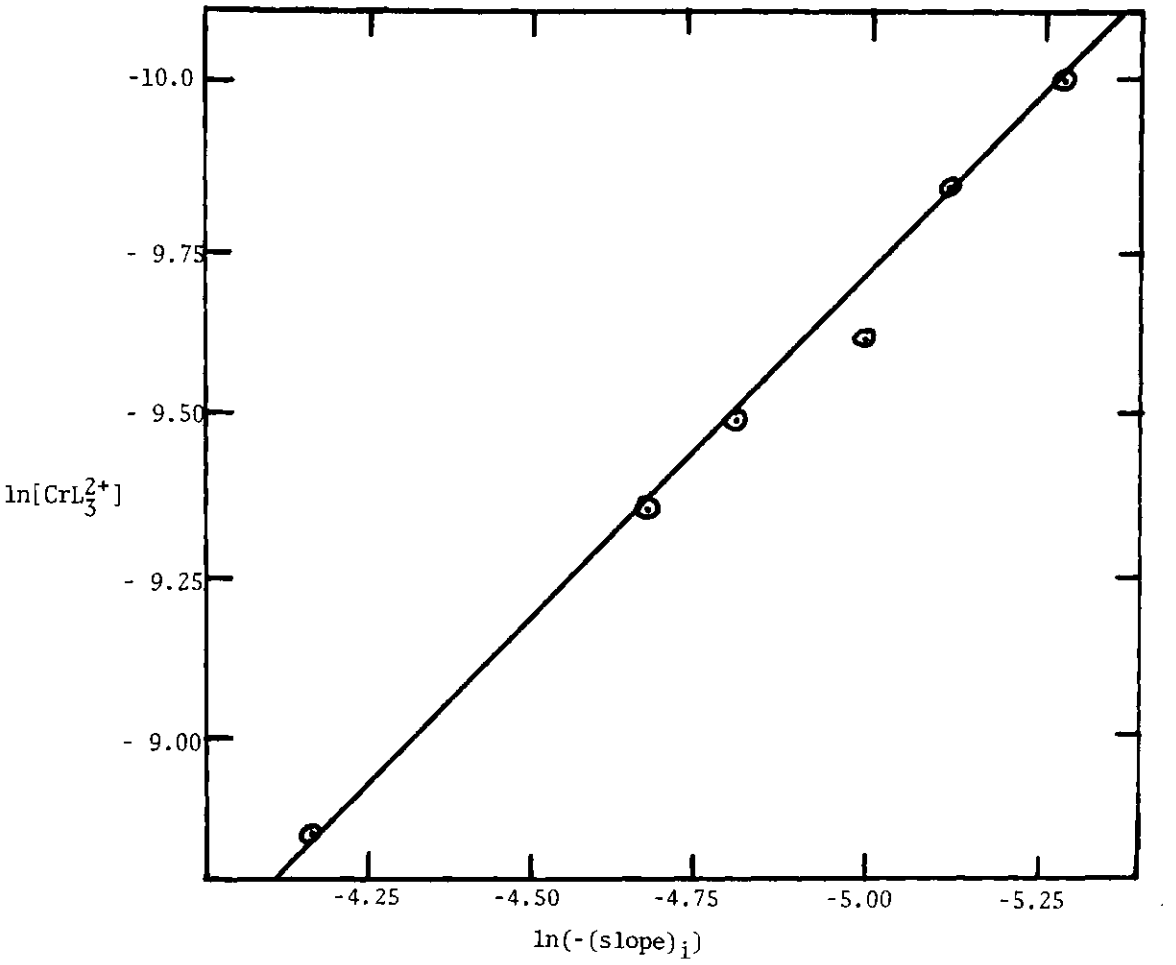

Figure 12. Order of CrL_3^{2+} for the Loss of Optical Activity

Due to experimental difficulties, the concentration of CrL_3^{2+} can not be kept constant so that a similar procedure cannot be used to determine n. However, since m was found to be equal to one, we can plot the $\ln(-(\text{slope})_i/[CrL_3^{2+}])$ versus the $\ln[CrL_3^{3+}]$ and the slope will be equal to n-1. Such a plot is shown in Figure 13 from the data in Table 6. The slope is found equal to -1, therefore n equals zero.

Substituting into Equation 26 the values of "m" and "n", yields:

$$\ln\alpha_t - \ln\alpha_i = -k_e[CrL_3^{2+}]t/[CrL_3^{3+}] \qquad (27)$$

k_e may now be evaluated from the initial slope of the $\ln\alpha_t$ versus time plots. Table 7 shows k_e found for various concentrations of the reactants in various concentrations of 1,10-phenanthroline. Table 8 shows k_e evaluated in various electrolytes and pH values.

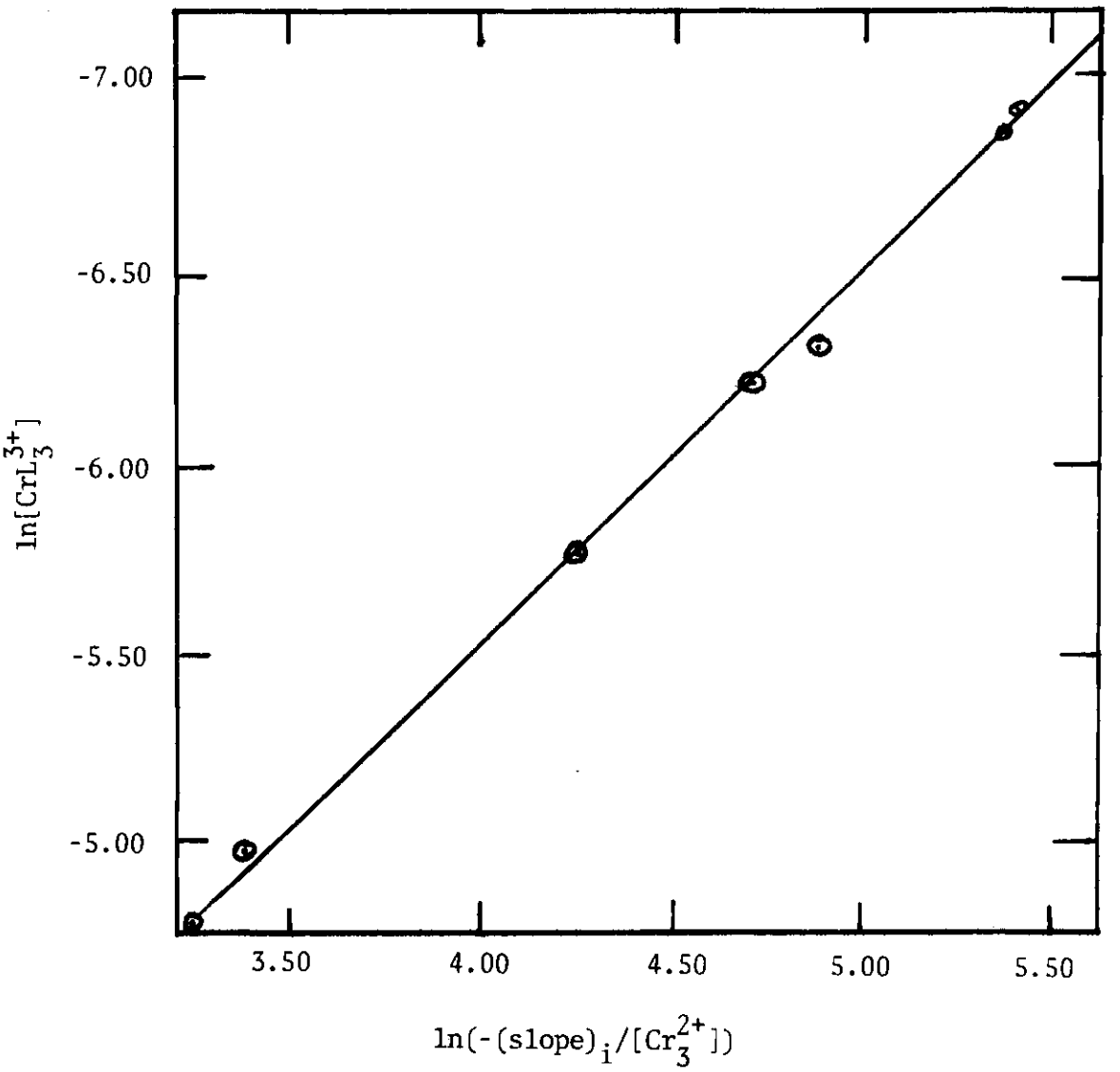

Figure 13. Order of CrL_3^{3+} for the Loss of Optical Activity

Table 6. Order of the Loss of Optical Activity with Respect to the $Cr(phen)_3^{3+}$ ion

Number of Samples	$Cr(phen)_3^{3+}$ x 10^3 M	$-\ln Cr(phen)_3^{3+}$	$-(slope)_i/CrL_3^{2+}$	$\ln -(slope)_i/CrL_3^{2+}$
2	8.25	+4.80	25.53	3.24
3	6.75	+5.00	29.08	3.37
5	3.09	+5.78	69.41	4.24
6	1.97	+6.23	109.9	4.70
2	1.82	+6.33	130.3	4.87
1	1.02	+6.89	212.7	5.36
1	0.943	+6.97	219.2	5.39

Table 7. Rate Constants, k_e and k_4 in Various 1,10-phenanthroline Solutions at 25.8°C

Number	$Cr(phen)_3^{2+}$ x 10^5 M	$Cr(phen)_3^{3+}$ x 10^3 M	Slope x 10^3	Phen x 10^2 M	k_e $Sec.^{-1}$	k_4 $Sec.^{-1}$
1	5.37	1.97	5.996	.927	.220	.144
2	6.71	1.97	6.78	.927	.200	.124
3	8.67	1.97	9.37	.927	.213	.137
4	7.60	1.97	8.22	.927	.213	.137
5	4.56	1.97	4.99	.927	.216	.140
6	14.36	1.97	15.65	.927	.215	.139
7	4.23	1.02	8.96	.962	.216	.140
8	6.06	0.943	13.34	.927	.208	.132
9	10.22	1.78	12.80	.863	.223	.147
10	8.53	3.09	5.66	.760	.205	.129
11	5.28	3.09	3.59	.760	.210	.134
12	9.96	3.09	7.48	.760	.232	.156
13	7.96	3.09	5.59	.760	.217	.141
14	6.63	3.09	4.48	.760	.209	.133
15	8.73	8.25	2.36	1.00	.207	.131
16	11.57	8.25	2.86	1.00	.204	.128
17	8.72	6.75	2.46	1.00	.191	.115
18	18.02	6.75	5.34	1.00	.200	.124
19	6.00	6.75	1.74	1.00	.196	.128
20	6.78	4.98	2.70	1.00	.198	.122
21	11.39	4.98	4.64	1.00	.203	.127
22	5.42	1.82	5.94	1.00	.199	.123
23	7.49	1.82	8.52	1.00	.207	.131

Table 8. Rate Constants, k_e and k_4, in Various Media

Number	$Cr(phen)_3^{2+}$ x 10^5 M	$Cr(phen)_3^{3+}$ x 10^3 M	Medium*	k_e $Sec.^{-1}$	k_4 $Sec.^{-1}$
1	12.5	2.09	0.01M $NaClC_4$, 0.01M phen	0.26	0.18
2	9.54	2.10	0.01M $NaClO_4$, 0.01M phen	0.24	0.16
3	6.51	2.21	0.01M $NaClO_4$, 0.01M phen	0.22	0.14
4	6.26	2.21	0.01M $NaClO_4$, 0.01M phen	0.23	0.15
5	5.44	2.21	0.01M $NaClO_4$, 0.01M phen	0.23	0.15
6	7.10	2.17	0.01M $NaClO_4$, 0.01M phen	0.22	0.14
7	8.37	2.17	0.01M $NaClO_4$, 0.01M phen	0.24	0.16
8	7.77	2.17	0.01M $NaClO_4$, 0.01M phen	0.22	0.14
9	6.73	1.50	0.01M $NaClO_4$, 0.01M phen	0.22	0.14
10	5.65	1.47	0.01M $NaClO_4$, 0.01M phen	0.21	0.13
11	7.53	1.80	0.01M $NaClO_4$, 0.01M phen	0.20	0.12
12	7.20	1.51	0.01M $NaClO_4$, 0.01M phen	0.22	0.14
13	6.54	1.19	0.01M $NaClO_4$, 0.01M phen	0.24	0.16
14	8.17	1.96	0.01M KCl, 0.01M phen	0.21	0.13
15	6.66	1.96	0.01M KCl, 0.01M phen	0.23	0.15
16	8.18	1.96	HCl; pH=4.20, 0.01M phen	0.191	0.115
17	7.78	1.96	HCl; pH=4.20, 0.01M phen	0.202	0.126

*The chromium(III) analysis on the $NaClO_4$ sample is questionable. The analysis was performed by base addition and peroxide oxidation of Cr(III) to Cr(VI). See Experimental Section for discussion.

CHAPTER IV

DISCUSSION

The Dissociation and Hydrolysis Reactions

The rate constant for the dissociation of $Cr(phen)_3^{2+}$ was found to be 0.083 $sec.^{-1}$ at 26.5°C by two separate experimental procedures. The agreement between the experimental procedures was excellent but fortuitous since the acid dissociation measurements were made at "room temperature" and were uncorrected for any heat evolved upon mixing. Basolo and Pearson[69] have discussed the rate of dissociation for the diimines of the first series transitional metals in terms of Hugh's Crystal Field Activation Energy. The value of 22.3 Kcal./mole for the activation energy agrees with the prediction for a low spin d^4 divalent metal ion.

The previous reported value of 0.015 $sec.^{-1}$ at 25°C for the dissociation reaction, determined in an electrochemistry experiment, is in error.[61] The error is believed to have occurred because the authors were unaware that adsorption phenomena were occurring, thereby invalidating their calculation of the rate constant.

It is possible to set a lower limit for the rate constant k_3 for the reaction between $(Cr(phen)_2(H_2O)_2)^{2+}$ and $Cr(phen)_3^{3+}$ using the equilibrium data of Hunt[54] and the inequality $k_3[CrL_3^{3+}] >> k_2[L]$. The rate constant k_2 is calculated to be 1.3×10^4 1/mole sec. and the lower limit for k_3 is calculated to be 10^6 1/mole sec. This value appears to be

reasonable, considering that a t_{2g} electron is being transferred to a t_{2g} orbital.

Loss of Optical Activity

The following mechanism is proposed to explain the fact that the rate of exchange between the tris 1,10-phenanthroline complexes of Cr(II) and Cr(III) was found to be zero order in Cr(III) and first order in Cr(II).

$$Cr(II) \underset{k_5}{\overset{k_4}{\rightleftharpoons}} Cr(II)^* \tag{28}$$

$$Cr(II)^* + Cr(III) \xrightarrow{k_6} \text{Exchange} \tag{29}$$

assuming a steady state of $Cr(II)^*$

$$-\frac{d[Cr(III)]}{dt} = \frac{k_4 k_6 [Cr(II)][Cr(III)]}{k_5 + k_6[Cr(III)]} \tag{30}$$

if $k_6[Cr(III)]$ is much greater than k_5, then

$$\frac{d[d\text{-}Cr(III)]}{dt} = -k_4[Cr(II)] \tag{31}$$

It is shown in Appendix 2 that the initial rate of change of reaction with time can be expressed as

$$\frac{d\alpha}{dt} = -\frac{\alpha(k_4 + k_1)[Cr(II)]}{Cr(III)} \tag{32}$$

when hydrolysis and the rate of exchange between the tris complexes are both considered and the Cr(II) is assumed to be constant. Integration of Equation 32 yields

$$\ln\alpha_t - \ln\alpha_i = \frac{(k_4 + k_1)[Cr(II)]t}{Cr(III)} \qquad (33)$$

From the initial slope of a plot of $\ln\alpha_t$ versus time, $k_4 + k_1$ may be calculated. From Appendix 2 we see that $k_e = k_4 + k_1$. Using the k_1 found from the hydrolysis data we may calculate k_4.

Tables 7 and 8 show the calculation of k_4 in various media. Table 9 shows k_4 found at various temperatures and the plot of the ln k_4 versus 1/T is shown in Figure 14. An activation energy of 27.2 Kcal./mole is calculated using a least squares statistical treatment. Using the assumptions stated previously for the calculation, an entropy of activation is found to be 28 cal./deg. mole.

In the above mathematical treatment it was assumed that the activation of $Cr(phen)_3^{2+}$ was the rate determining step. The occurance of a prior activation of one of the reactants in an exchange reaction is rare. Gorton[38] has presented a similar mechanism for the $Co(phen)_3^{2+}$/ $Co(phen)_3^{3+}$ exchange. He suggested that the activated $Co(phen)_3^{2+}$ complex is either an electronically excited state or an intermediate formed from catalytic impurities reacting with the $Co(phen)_3^{2+}$.

The activation of $Cr(phen)_3^{2+}$ to an electronically excited state by a d-d transition would not be expected to facilitate the electron transfer. Since in the ground state all the electrons are in a t_{2g}

Table 9. Rate of Exchange at Various Temperatures in 0.01 M 1,10-phenanthroline

Number of Samples	k_4	$-\ln k_4$	Temperature K°	Reciprocal of Temperature $°K^{-1} \times 10^3$
4	0.022	3.817	287.65	3.473
4	0.056	2.882	292.95	3.413
5	0.134	2.010	298.95	3.345
5	0.410	0.892	305.95	3.269

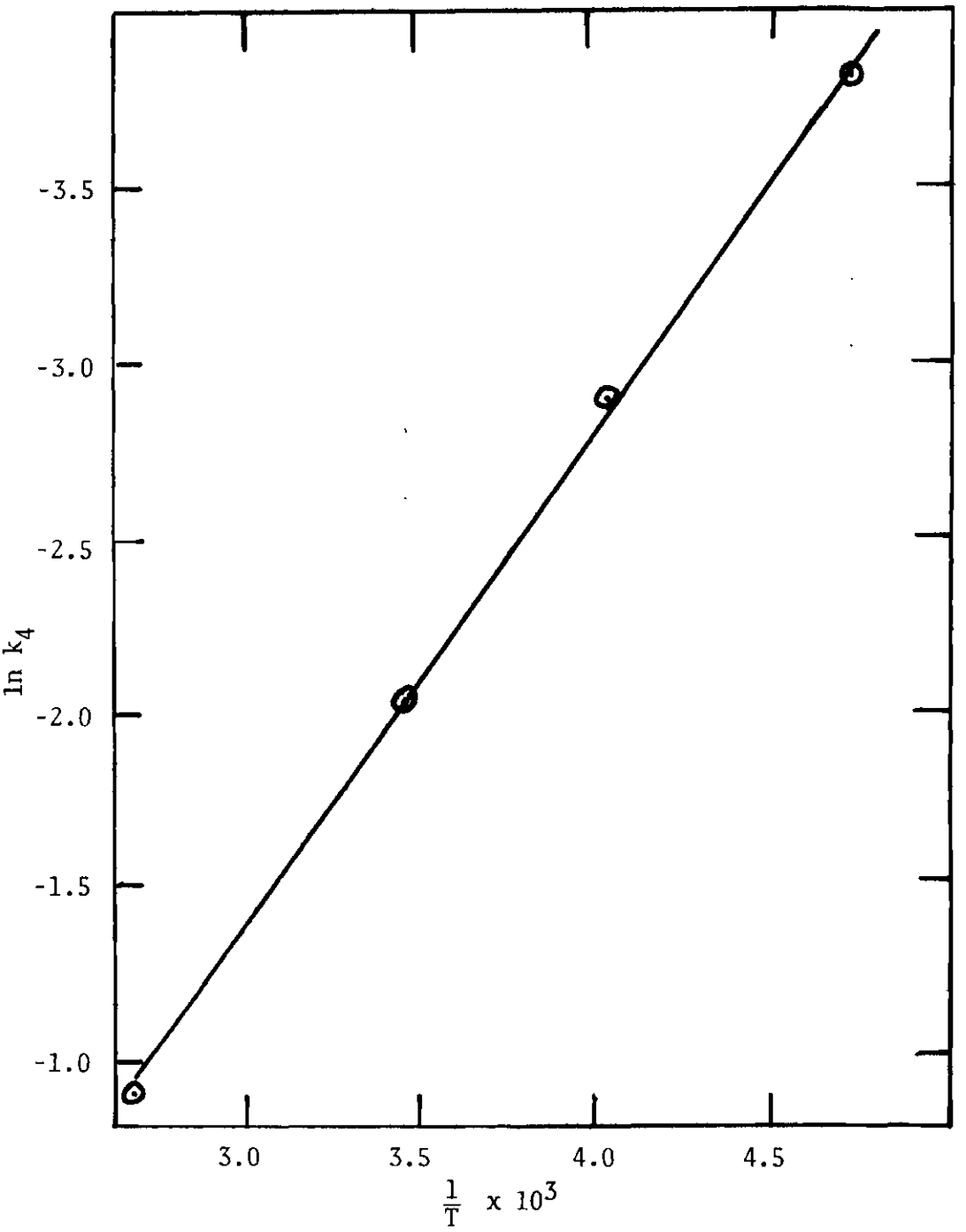

Figure 14. Activation Energy of the Exchange Reaction between Tris-(1,10-phenanthroline)chromium(II) and Tris(1,10-phenanthroline)chromium(III).

orbital, electronic excitation would lead to exciting a t_{2g} electron to an e_g orbital. As discussed in the introduction, such an excitation would be expected to decrease the rate of the reaction.

Konig and Herzog[47] have reported two relatively narrow absorption bands for $Cr(bipy)_3^{2+}$ in the near infrared at 8700 cm^{-1} (ε=10,000) and 9,900 cm^{-1} (ε=2,900) and tentatively assigned them as charge transfer bands. Broad bands at higher energies, e.g., 12,050 cm^{-1} (ε=1,700), and 14,550 cm^{-1} (ε=2,300), were assigned as transitions having some charge transfer character and some d-d character. Fujita et al.[46] measured the spectra of both $Cr(bipy)_3^{2+}$ and $Cr(phen)_3^{2+}$. Bands at 8,500 cm^{-1} and 12,500 cm^{-1} were assigned to metal to ligand charge transfer transitions. The less intense band at 9,900 cm^{-1} appears in both of the spectra but was not discussed. The band at 12,500 cm^{-1} was observed by this author to be very wide with a maximum at 12,340 cm^{-1}. The energies corresponding to 8,700 cm^{-1} and 9,900 cm^{-1} are 24.9 and 28.3 respectively. The activation energy for the electron transfer reaction, 27.2 Kcal./mole, is within experimental error of the energies of the first two charge transfer bands. This correspondence suggests that the reaction is occurring by thermal activation to one or both of these excited states. Analogous absorption bands, but at higher energies, are observed in the $V(bipy)_3^{2+}$ and $Fe(bipy)_3^{2+}$ complexes[46], and also in the $Ru(bipy)_3^{2+}$ complex.[71] These authors[46,71] assign the transitions as $d \rightarrow \pi^*$ (i.e., metal $\rightarrow$ ligand) charge transfer.

If the excited states observed in absorption are the reaction intermediates in the exchange reaction they must have sufficiently long life-time to satisfy the observed kinetics. In particular, the

inequality,

$$k_6[Cr(III)] >> k_5$$

assumed in the evaluation of k_4, must be true. Estimating a value of 10^{10} 1./mole sec. for k_6* and a concentration of Cr(III) of 10^{-3}M, we calculate $10^7 >> k_5$. A value of less than 10^6 sec.$^{-1}$ is required. Nothing is known about the life-times of these states in the Cr(II) complexes, but the analogous charge transfer absorption in $Ru(bipy)_3^{2+}$ leads to an excited state exhibiting phosphorescence. The rate constant for phosphorescent emission is 3×10^5 sec.$^{-1}$. The assumption of an excited state of $Cr(phen)_3^{2+}$ with sufficient life-time to undergo exchange is thus not unreasonable.

A second possibility for the nature of the activated $Cr(phen)_3^{2+}$ is suggested by the work of La Mar and Van Hecke.[40] They have proposed that water molecules are bound in a secondary coordinated sphere of tris methyl and ethyl substituted 1,10-phenanthroline complexes of chromium(II), and probably in the unsubstituted complex, in a different way as compared to nickel(II), cobalt(II) and iron(III) substituted 1,10-phenanthroline complexes, but similar to the iron(II) complexes. Estimating the ionic radius for the tris(4,7-dimethyl-1,10-phenanthroline(chromium(II) complex at 7Å, they proposed penetration of approxi-

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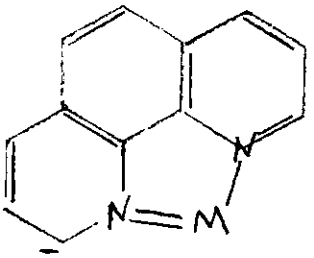
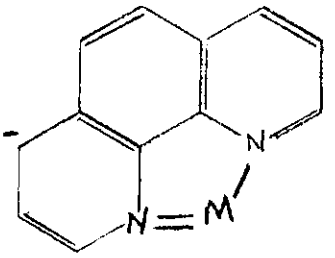
*The value of 10^{10} 1./mole sec. for k_6 is an estimation of the rate constant for a diffusion controlled bimolecular reaction involving metal complexes, see Table 2 and ref. 15.

mately 2Å by water molecules into the pockets between the "propellor blades" of the phenanthroline ring systems. The water molecules are not bound to the chromium(II), but are believed held in position by hydrogen bonding. The significant pi back bonding of the $Cr(phen)_3^{2+}$ ion leads to the delocalized negative charge being centered at the 4 and 7 positions of the 1,10-phenanthroline. Resonance structures for this type of bonding can be written as



(I)



(II)

The resonance structures related by a two-fold axis are omitted. Structure II is expected to make a significant contribution to the ground state for the Cr(II) and Fe(II) complexes. It is pictured that the water is electrostatically attracted to the partial charge at the 4 and 7 positions. The results of nmr experiments show two types of protons in the solvent; one is outside the estimated ionic radius at 7Å and the other is inside the ionic radius. When the solvent is changed to methanol only the protons outside the ionic radius of 7Å are detected.

The activated complex for $Cr(phen)_3^{2+}$ is proposed to be the removal or the rearrangement of the water molecules in the secondary coordination sphere. The removal or rearrangement of the water molecules would permit much closer contact between the $Cr(phen)_3^{2+}$ and $Cr(phen)_3^{3+}$. Also the removal of the water molecules that are held in the 4 and 7 positions of $Cr(phen)_3^{2+}$ would present a favorable site for an electron transfer with $Cr(phen)_3^{3+}$. The loss of the highly ordered arrangement of water molecules in the activated intermediate is probably responsible for the large entropy of activation, 28 cal./mole deg. The inequality, $k_6[Cr(III)] >> k_5$, again applies requiring that k_5 be less than 10^6 sec.$^{-1}$. There is no reliable basis at the present time for estimating whether or not this condition is satisfied. La Mar and Van Hecke[40] have been unable to establish a meaningful equilibrium constant for the exchange of water molecules between those that are bound between the 1,10-phenanthrolines and those that are unbound.

One proposal that can not be tested is that the exchange between $Cr(phen)_3^{2+}$ and d-$Cr(phen)_3^{3+}$ is stereospecific. Sutter and Hunt[28] have reported such a stereospecific reaction between $Co(phen)_3^{3+}$ and $Cr(phen)_3^{2+}$. In the $Cr(phen)_3^{2+}$ - $Cr(phen)_3^{3+}$ reaction, the lack of a dependence on $Cr(phen)_3^{3+}$ makes this pathway unlikely.

APPENDIX I

The absorbance at any time is equal to:

$$A_t = be[Cr(phen)_3^{2+}] + be_p[phen] \quad (1)$$

where:

b = path length of the cell

e = extinction coefficient of $Cr(phen)_3^{2+}$

e_p = extinction coefficient of 1,10-phenanthroline

At infinite time, the absorbance is equal to

$$A\infty = be_p[phen] \quad (2)$$

and Equation 1 can be written:

$$A_t - A_\infty = be[Cr(phen)_3^{2+}] \quad (3)$$

At time equal zero, the initial absorbance is equal to A_i

$$A_i = be[Cr(phen)_3^{2+}]_i + be_p[phen] \quad (4)$$

using Equation 2

$$A_i - A_\infty = be[Cr(phen)_3^{2+}]_i \quad (5)$$

Solving Equation 3 and 5 and substituting into Equation 11 from the text:

$$\ln\left(\frac{A_t - A_\infty}{A_i - A_\infty}\right) = -k_1 t \qquad (6)$$

Rearranging Equation 6,

$$\ln(A_t - A_\infty) - \ln(A_i - A_\infty) = -k_1 t \qquad (7)$$

APPENDIX 2

Let d-$[Cr(phen)_3^{3+}]$ = x α = degrees of rotation

1-$[Cr(phen)_3^{3+}]$ = 1 c = conversion constant for converting mole/l. of $Cr(phen)_3^{3+}$ into degrees

$[Cr(phen)_3^{2+}]$ = b

total $[Cr(phen)_3^{3+}]$ = a

For any degree of rotation:

$$\alpha = c(x-1) \tag{1}$$

Taking the time derivative:

$$\frac{d\alpha}{dt} = c\left(\frac{dx}{dt} - \frac{dl}{dt}\right) \tag{2}$$

The change in x is due to the rate of hydrolysis and the rate exchange

$$-\frac{dx}{dt} = \frac{x}{a}\frac{k_4 b}{2} - \frac{l}{a}\frac{k_4 b}{2} + \frac{x}{a}k_1 b \tag{3}$$

Similarly for l

$$-\frac{dl}{dt} = \frac{l}{a}\frac{k_4 b}{2} - \frac{x}{a}\frac{k_4 b}{2} + \frac{l}{a}k_1 b \tag{4}$$

Then for $-d\alpha/dt$, we obtain by substituting Equation 3 and 4 into Equation 2:

$$-\frac{d\alpha}{dt} = c\left(\frac{x}{a}k_4 b - \frac{l}{a}k_4 b + \frac{x}{a}k_1 b - \frac{l}{a}k_1 b\right) \tag{5}$$

$$- \frac{d\alpha}{dt} = c\left(\frac{k_4 b(x-1)}{a} + \frac{k_1 b(x-1)}{a}\right) \tag{6}$$

Using Equation 1 and rearranging:

$$- \frac{d\alpha}{dt} = \frac{\alpha\, b(k_4+k_1)}{a} \tag{7}$$

REFERENCES

1. H. Taube, Advances in Inorg. Chem. Radiochem., 1, 1 (1959).

2. F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions, 2nd Ed., John Wiley and Sons, Inc., New York, 1968, p. 466.

3. H. Taube, Electron Transfer Reactions of Complex Ions in Solution, Academic Press, New York, 1970.

4. D. Benson, Mechanism of Inorganic Reactions in Solution, McGraw-Hill Publishing Co., New York, 1969, p. 95.

5. N. Sutin, Electrochimica Acta, 13, 1175 (1968).

6. R. A. Marcus, Ann. Rev. Phys. Chem., 15, 155 (1964).

7. R. A. Marcus, J. Phys. Chem., 67, 853 (1963).

8. V. G. Levich, Adv. Electrochem. and Electrochem. Engr., 4, 249 (1966).

9. N. S. Hush, Trans. Faraday Soc., 57, 557 (1961).

10. E. Dacher and K. J. Laidler, Modern Aspects of Electrochemistry, 3, 1 (1964).

11. R. G. Linck, Transitional Metals in Homogeneous Catalysis, Ed. G. N. Schrauzer, Marcel Dekker, Inc., New York, 1971, p. 298.

12. See reference 2 p. 475 and p. 481.

13. See reference 2 p. 465.

14. P. G. Rasmussen and C. H. Brubaker, Jr., Inorg. Chem., 3, 977 (1964).

15. See reference 2, Chapter 6.

16. J. F. Endicott, R. R. Schroeder, D. H. Chidester, and D. R. Ferrier, J. Phys. Chem., 77, 2579 (1973).

17. N. E. Kime and J. A. Ibers, Acta Crystallogr., Sect. B, 25, 168 (1969).

18. H. C. Stynes and J. A. Ibers, Inorg. Chem., 19 2304 (1971).

19. See reference 2 p. 512.

20. J. T. Yardley and J. K. Beattie, J. Amer. Chem, Soc., 94, 8925 (1972).

21. J. K. Beattie, N. Sutin, D. H. Turner and G. W. Flynn, J. Amer. Chem. Soc., 95, 2052 (1973).

22. M. D. Glick, J. M. Kuszaj, and J. F. Endicott, J. Amer. Chem. Soc., 95, 5097 (1973).

23. R. G. Inskeep and L. Bjerrum, Acta Chem. Scand., 15, 62 (1961).

24. A. M. Zwickel and H. Taube, Disc. Faraday Soc., 29, 42 (1960).

25. J. P. Candlin, J. Halpern and D. L. Trimm, J. Amer. Chem. Soc., 86, 1019 (1964).

26. J. K. Beattie and F. Basolo, Inorg. Chem., 6, 2069 (1967).

27. R. Farina and R. G. Wilkins, Inorg. Chem., 7, 514 (1968).

28. J. H. Sutter and J. B. Hunt, J. Amer. Chem. Soc., 91, 3107 (1969).

29. A. Anderson and N. A. Bonner, J. Amer. Chem. Soc., 76, 3826 (1954).

30. D. R. Stranks, Disc. Faraday Soc., 29, 73 (1960).

31. A. Earnshaw, L. F. Larkworthy, K. C. Patel, R. L. Carlin, and E. G. Terezakis, J. Chem. Soc., A, 511 (1966).

32. W. B. Lewis, C. D. Coryell, and J. W. Irivne, J. Chem. Soc., Supplementary Issue No. 2, s-386 (1949).

33. F. F. Dwyer and A. M. Sargeson, Nature, 187, 1022 (1960).

34. A. W. Adamson and K. S. Vorres, J. Inorg. Nucl. Chem., 3, 206 (1956).

35. Y. A. Im and D. H. Busch, J. Amer. Chem. Soc., 83, 3357 (1961).

36. E. Eichler and A. C. Wahl, J. Amer. Chem. Soc., 80, 4145 (1958).

37. M. W. Dietrich and A. C. Wahl, J. Chem. Phys., 38, 1591 (1963).

38. E. M. Gorton, Thesis, Ga. Inst. of Tech., 1965.

39. C. S. Lee, E. M. Gorton, H. M. Neumann, and H. R. Junt, Jr., Inorg. Chem., 5, 1397 (1966).

40. G. N. La Mar and G. R. Van Hecke, J. Amer. Chem. Soc., 94, 9049 (1972).

41. N. A. P. Kane-Maguire, B. Dunlop and C. H. Langford, J. Amer. Chem. Soc., 93, 6293 (1971).

42. W. R. McWhinnie and J. D. Miller, Adv. in Inorg. Chem., 12, 135 (1969).

43. C. S. Garner and D. A. House, Trans. Metal Chem., 6, 59 (1970).

44. J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire and H. Lipp, Inorg. Chem., 8, 771 (1969).

45. S. F. Mason and B. J. Peart, Inorg. Chem., 12, 949 (1973).

46. I. Fujita, I. Yazaki, Y. Torii and H. Kobayashi, Bull. Chem. Soc. Japan, 45, 2156 (1972).

47. E. Konig and S. Herzog, J. Inorg. Nucl. Chem., 32, 585 (1969).

48. E. G. Terezakis and R. L. Carlin, Inorg. Chem., 6, 2125 (1967).

49. Y. M. Udachin and M. E. Dyatkina, J. Struct. Chem., 8, 325 (1967).

50. P. M. Lutz, G. J. Long and W. A. Baker, Inorg. Chem., 8, 2529 (1969).

51. G. N. La Mar and G. R. Van Hecke, J. Amer. Chem. Soc., 91, 3442 (1969).

52. G. N. La Mar and G. R. Van Hecke, J. Amer. Chem. Soc., 94, 9042 (1972).

53. G. N. La Mar, J. Amer. Chem. Soc., 94, 9055 (1972).

54. H. R. Hunt, Jr., private communications.

55. H. Irving and D. P. Mellor, J. Chem. Soc., 5222 (1962).

56. A. A. Vleck, Nature (London), 189, 393 (1961).

57. B. R. Baker and B. DevMehta, Inorg. Chem., 4, 848 (1965).

58. B. V. Tucker, J. M. Fitzgerald, L. G. Hargis and L. B. Rogers, J. Electro. Anal. Chem., 13, 400 (1967).

59. J. Candlon, J. Halpern and D. L. Trimm, J. Amer. Chem. Soc., 86 1019 (1964).

60. D. M. Soignet and L. G. Hargis, Inorg. Chem., 11, 2349 (1972).

61. D. M. Soignet and L. G. Hargis, Inorg. Chem., 11, 2921 (1972).

62. W. McCray and P. Sturrock, private communications.

63. D. Wolcott and J. B. Hunt., Inorg. Chem., 7, 755 (1968).

64. R. G. Inskeep and M. Benson, J. Inorg. Nucl. Chem., 20, 290 (1961).

65. R. B. Fischer and D. G. Peters, Basic Theory and Practice of Quantitative Chemical Analysis, W. B. Saunders, Philadelphia, 1968, p. 662.

66. C. H. Grogan, H. J. Cahnmann and E. Lethco, Anal. Chem., 27, 983 (1955).

67. G. W. Haupt, J. Res. Nat. Bureau Stand., 48, 414 (1952).

68. D. F. Shriver, The Manipulation of Air-Sensitive Compounds, Mc-Graw Hill Book Company, New York, 1969.

69. See reference 2, p. 155.

70. H. M. Neumann, private communications.

71. F. E. Lytle and D. M. Hercules, J. Amer. Chem. Soc., 91, 253 (1969).

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